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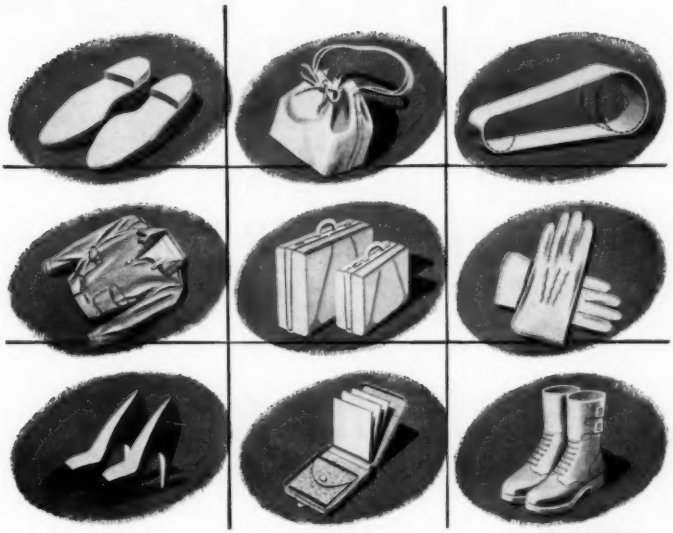

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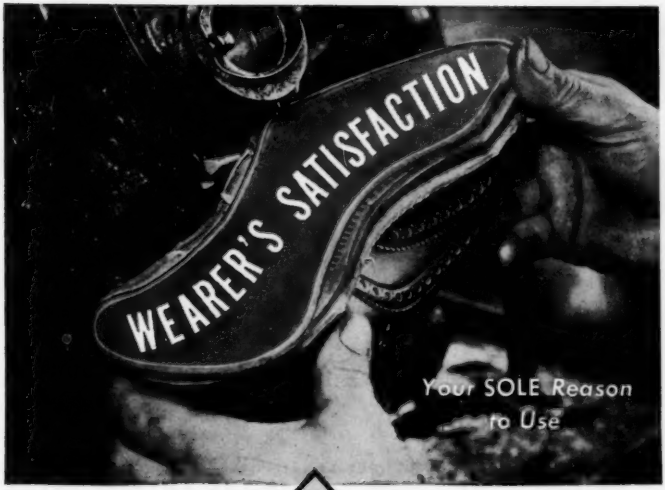

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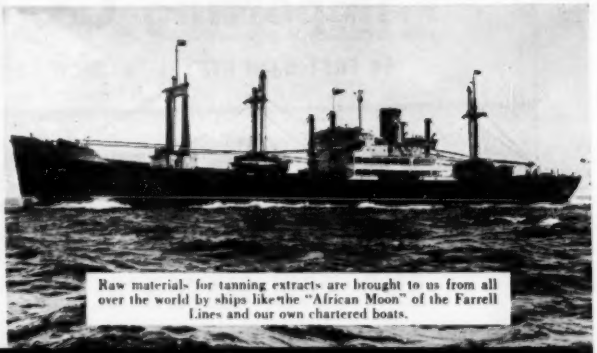

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AMERICAN LEATHER CHEMISTS ASSOCIATION

Vol. L MAY 1955 No. 5

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Douglas McCandlish—Obituary

Professor Douglas McCandlish died at his home in Leeds, England, December 18, 1954, at the age of seventy-one. He has been well known in leather chemistry for approximately fifty years. About twelve of those years were spent as chief chemist for A. F. Gallun and Sons, Inc. of Milwaukee, Wisconsin. As a member of the English Society of Leather Trades' Chemists and an honorary member of the American Leather Chemists Association he was interested in the activities of chemists in this field all over the world. In 1927 he presided at an international meeting held in London. Many of his numerous contributions were published in the Journal of the American Leather Chemists Association. It was during his sojourn in America that he wrote the article "Precipitation Point Control of Chrome Tanning Liquors", one of his best known publications. With Professor Procter, he was co-author of the "Procter-McCandlish Method of Determining the Basicity of Chrome Tanning Liquors.

In spite of his reputation for strictest scientific discipline in his work, Professor McCandlish was essentially kindly and very human in his dealings with his associates. This quality also expressed itself in an active participation in the affairs of the community. Retirement, which took place several years ago, had already deprived the industry of his active participation; but his example and prestige remained. His name will hold a place of honor in the history of leather chemistry.

The Color of Dyed Leather*

By GEORGE STRAUSS**, ROBERT STUBBINGS and (MRS.) DOROTHY NEMES

Division of Leather Technology
Chemistry Department
Lehigh University
Bethlehem, Pa.

SUMMARY

The numerical definition and instrumental methods of measuring surface color are reviewed. Behavior of a dye in leather dyeing is described using the concepts of dye locus and coloring efficiency. The dye locus is found to be constant under a wide vriety of conditions while coloring efficiency is easily affected by variation in the leather or the method of dyeing. This rationalization makes possible the prediction of colors obtainable with a given dye.

The dye locus for a given dye is constant on various leathers and under a variety of dyeing conditions. It is changed only if:

*Presented at the American Leather Chemists Association, June 8, 1954 at Bedford Springs, Pa.
**Presented to the Graduate Faculty of Lehigh University as partial requirement for a Graduate Thesis.

1. The dye itself changes color with pH,
2. Any other coloring matter (e. g. vegetable tannin) is added, or
3. The degree of aggregation of the dye is changed.

The coloring efficiency of a given dye is highly variable. It depends on:

1. Inherent coloring power, and
2. Degree of penetration which is sensitive to minute changes in the leather and/or dyeing conditions.

Introduction

The operation of dyeing leather to match a given color standard as practiced in the average tannery is very largely a matter of trial and error. Not only has the desired color to be approached by successive test dyeings and adjustments, but in addition there is frequent disagreement among colorists as to what constitutes a "color match". Under these conditions there is a definite need to know more of the underlying principles of leather dyeing and in particular how each variable in raw material and in the process itself affects the final color of the leather. Further, a system of specifying colors numerically has to be adopted so that the effect of these variables may be discussed quantitatively.

Vickerstaff [1] has discussed the physical chemistry of dyeing in great detail, in terms of dye migration into the fiber material. This work, although of great importance, refers to equilibrium conditions and to a homogeneous fiber material. Both conditions apply to textile dyeing but not to the dyeing of leather. Otto [2] has investigated the affinity of dyes for leather by considering both electrostatic interaction and dispersion forces between dye ions and the charged leather surface. The degree of penetration of dyes, and methods for measuring it have received the attention of several workers [2], [3]. However, none of the papers mentioned has anything to say about the surface color resulting from the dyeing. In view of this the present work was undertaken. As will be shown, the relationship between surface color and the amount of dye used, type of leather and choice of process variables can be formulated by some generally applicable rules.

The Nature of Color

The principles of numerical specification of color and of color measurement by machines are well understood [4]; for convenience they will be briefly reviewed here. The color of a surface is uniquely defined in the *physical* sense by its spectrophotometric reflection curve, measured under such conditions that specular reflection i. e. gloss, is excluded. Such a curve shows the percentage of incident light reflected at each wavelength. This physical measurement is made by a spectrophotometer. The reflectance curve as such is of little interest since it is only indirectly related to the color actually seen by the observer. The purely physical measurements can be converted to those of

sensation by first allowing for the variable sensitivity of the eye for light of different wavelengths (being greatest for yellow, and falling off both towards red and violet) and secondly by defining three arbitrary primary colors chosen in such a way that any color whatever can be made up from them.

The color *as perceived* can now be defined by three numbers, stating the relative amounts of the three arbitary primaries. These three numbers are known as the C. I. E. Tristimulus Values (after the International Commission on Illumination of 1931 which defined the three primaries) [4c].

The tristimulus values can be obtained from the reflectance curve by a process of integration. The calculation is laborious, but an automatic integrator is available (although very expensive). The tristimulus values, although an exact definition of the given color, give no idea (except to the specialist) what the color really looks like.

Systems of organizing actual color chips into an arrangement have been used for a long time. One of the industrially used systems is that devised by Munsell [9]. It is found that a three-dimensional array must be used for such a color system, known as the color space. The reason for this is that a color possesses three attributes: lightness, hue and saturation. These terms are best explained by means of the color space shown in Figure 1.

The space is seen to have a central vertical axis which contains all the achromatic (i. e.-gray) colors. This vertical axis is the *lightness* scale, ranging from black at the bottom (0 per cent lightness) through the various grays to white at the top (100 per cent lightness).

The various spectrum colors of a given lightness are arranged in a circle about the lightness axis. Consider for example the circle shown at the 50 per cent lightness level. Going out from the center of this circle in the direction towards red, we obtain a series of colors all of the same *hue* (red in this case) and of increasing *saturation*, ranging from zero saturation at the center (= grey) to the maximum saturation, or vividness, at the periphery of the circle.

From the point representing the fully saturated red we may go up or down in a vertical direction and obtain a range of colors all of the same hue and saturation but differing in lightness. In this case the series would range from a light, vivid pink to a dark, vivid red. The same kind of relationship of course applies to other hues and other degrees of saturation.

We now have defined the color by giving the three coordinates of the point representing it in the color space. The great advantage of this method of defining a color is that the coordinates have a readily understood meaning. Tristimulus colorimeters are available now which can measure a color very rapidly (in a matter of seconds) and give the result directly as the three space-coordinates.

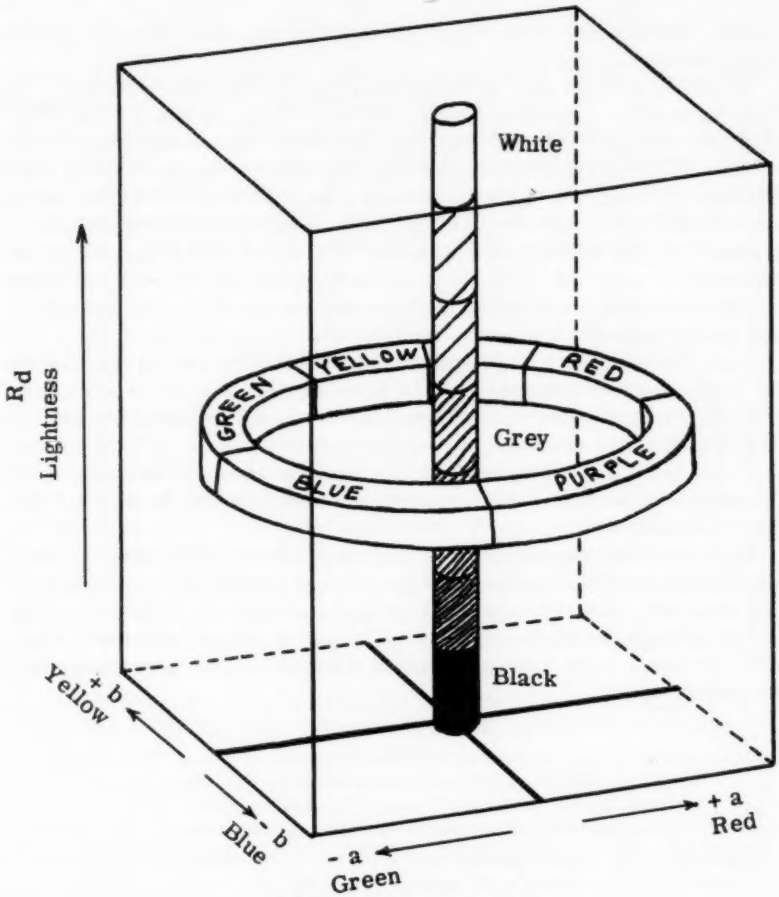


FIGURE 1.—The Color Solid.

Different color spaces may be constructed, using either cylindrical coordinates as in the system just described, or rectangular coordinates. Such rectangular coordinates are also shown in Figure 1. A highly desirable requirement of all color space systems is that they should be psychologically spaced, i. e. unit distance should represent the minimum color difference perceptible by the eye in all three directions. Actual color spaces in use only approach this ideal with varying degrees of success.

It will be noted that the three dimensional character of color manifests itself in that a color can be defined either by its tristimulus values (i. e. the relative amounts of three constituent primaries) or by its three space coordi-

nates. The tristimulus values can be converted by calculation into any desired coordinate system.

The color notation used in the present paper is that due to Hunter[6]. In this rectangular coordinate system, lightness is represented by the letter R_d. Hue and saturation together are expressed by the values of two coordinates *a* and *b* in a horizontal plane. Coordinate *a* represents redness when positive and greenness when negative; *b* indicates yellowness when positive and blueness when negative (See Figure 1). These coordinates must refer to a given light source, since the appearance of a colored surface depends on the illumination used. All results reported in this paper are referred to average northern daylight, since this is the illumination commonly used when matching leather colors.

From the foregoing it is clear that a color can be measured in terms of the Hunter notation by going through the following steps:

1. Determine the spectrometric curve by means of a spectrophotometer.
2. Calculate the tristimulus values X, Y, Z.
3. Convert X, Y, Z mathematically into the Hunter values R_d, *a*, *b*. Alternatively the Hunter values may be determined directly by some suitable filter colorimeter.

Table 1 shows the closeness of agreement obtainable between spectrophotometer and filter colorimeter for a series of leathers of a common dark red shoe color. Since the aim of the present study was to investigate trends rather than absolute values the agreement was considered sufficiently close, and the much more rapid colorimeter adopted for all subsequent color measurements.

TABLE I

Comparison of Spectrophotometer and Filter Colorimeter Readings (Two positions on each sample were read; the Hunter values under "Colorimeter" were read directly while those under "Spectrophotometer" were obtained from the tristimulus values by calculation)

Sample No.	Spectrophotometer			Colorimeter		
	Rd	*a*	*b*	*Rd*	*a*	*b*
1	5.0	45.0	13.3	5.4	47.0	11.8
	5.1	45.1	13.3	5.5	46.7	11.9
2	4.2	38.6	11.5	4.5	39.6	10.2
	4.3	39.1	11.3	4.5	39.1	10.0
3	4.2	38.4	11.2	5.7	37.8	10.1
	4.2	36.0	10.9	4.4	40.6	10.2
4	3.5	35.4	10.5	3.9	36.7	9.1
	3.8	35.5	10.5	4.1	36.0	9.0
5	4.2	38.3	11.5	4.9	37.4	9.4
	4.0	36.3	10.6	4.5	36.9	9.5
6	3.4	31.5	9.5	4.2	32.5	8.5
	3.5	32.4	9.6	4.2	32.2	8.5
7	3.5	31.9	9.7	4.4	32.5	8.6
	3.6	31.0	9.2	4.4	32.7	8.6

Experimental

A standard dyeing procedure was used throughout, chosen so as to approach typical tannery practice as closely as possible.

Various straight chrome tanned leathers (calf, side and kid) were received in the blue and cut up into 3″x3″ squares. These were washed and stored in the moist condition until used. All washings, dyeings, etc. were carried out in stoppered quart jars placed on a vertically reciprocating shaker oscillating about 120 rpm. This method effectively imitated the flexing and pounding action of the tanning drum.

Just prior to each dyeing a group of eight leather squares was neutralized with borax in such a way that the subsequent dye bath pH was between 3.8 and 4.2. The amount of borax had to be adjusted for each type of leather to achieve this uniform dyeing pH range. The pieces were neutralized for 30 minutes, then washed for 30 minutes after which they were dyed for 45 minutes at 50° C. The volume of dye float was 40 ml. for a 3″ x 3″ square. The amounts of dye for the eight samples of a series were 0.5, 1, 2, 3, 4, 6, 8 and 10 ounces of dye per 100 sq. ft. of leather. These quantities were either completely or almost completely exhausted. Where exhaustion was incomplete the residual amount of dye in the liquor was measured colorimetrically.

In some series the samples were treated with neutral syntan (1 per cent on weight of leather) or were vegetable mordanted (2 per cent quebracho on weight of leather) prior to dyeing. These steps were also done on the reciprocating shaker in a float volume of 40 ml. per square.

After dyeing, the samples were washed free of any uncombined dye, pressed and air-dried. Their color was then read on a filter colorimeter.

The Dye Locus

If a series of leather samples is dyed with progressively increasing amounts of the same dye (and all other conditions of dyeing being held constant) the surface colors obtained are found to change in a manner characteristic of that dye. If the colors are measured in terms of Hunter values and plotted in the color space, a series of points is obtained which can be joined by a smooth curve, as shown in Figure 2.

Such a curve is called a Dye Locus since it includes all the colors the dye is capable of producing. The concept of the dye locus is highly useful as by this means the behavior of a given dye can be discussed in a manner that is readily visualized.

The dye locus illustrated in Figure 2 is typical: As the amount of dye (the dye level) is increased there is a continual decrease in lightness, accompanied by a shift in hue while saturation at first increases to a maximum and then decreases at still higher dye levels. This means that the locus is shaped like

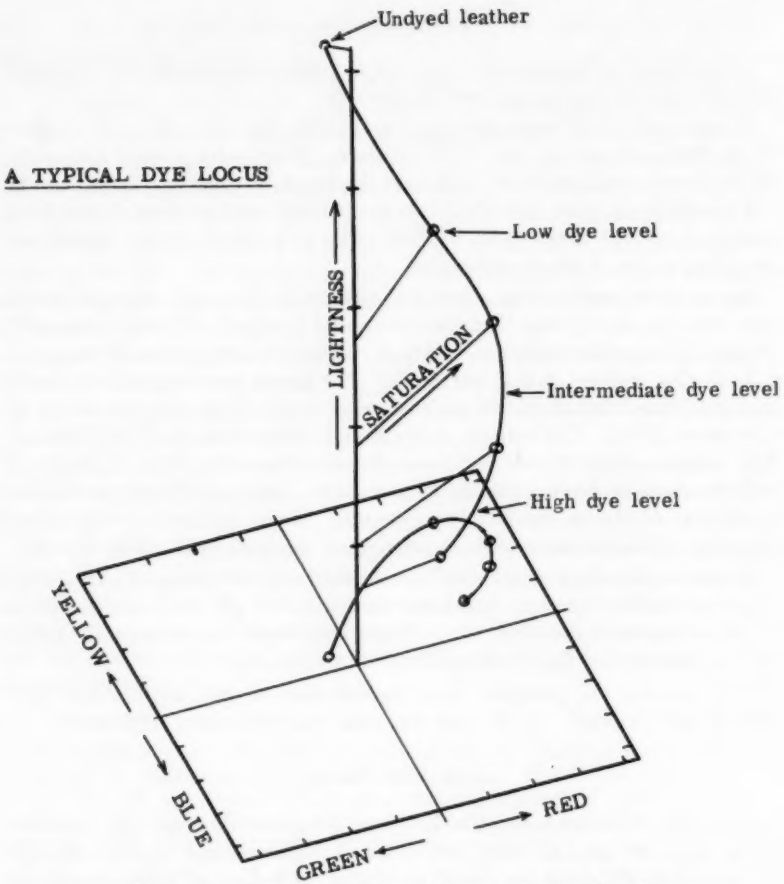


FIGURE 2.—A Typical Dye Locus, Shown in Perspective View.

a helix and that a given dye yields a series of distinctly different colors and not just "various depths" of the same color as one might have supposed. At the bottom of Figure 2, a plan view of the locus (i. e. a trace of the curve upon the *a-b* plane) is also shown, since loci will be represented by such plan views in the rest of this paper.

Instead of drawing a perspective view of the locus it is more convenient to show three separate views: A plan view (the *a-b* diagram) and two side views (the R_d-*a* and R_d-*b* diagrams), as illustrated in Figure 3.

That this general shape of dye loci is not confined to leather dyeing has been demonstrated by Stearns[7] who has reported similar dye behavior In

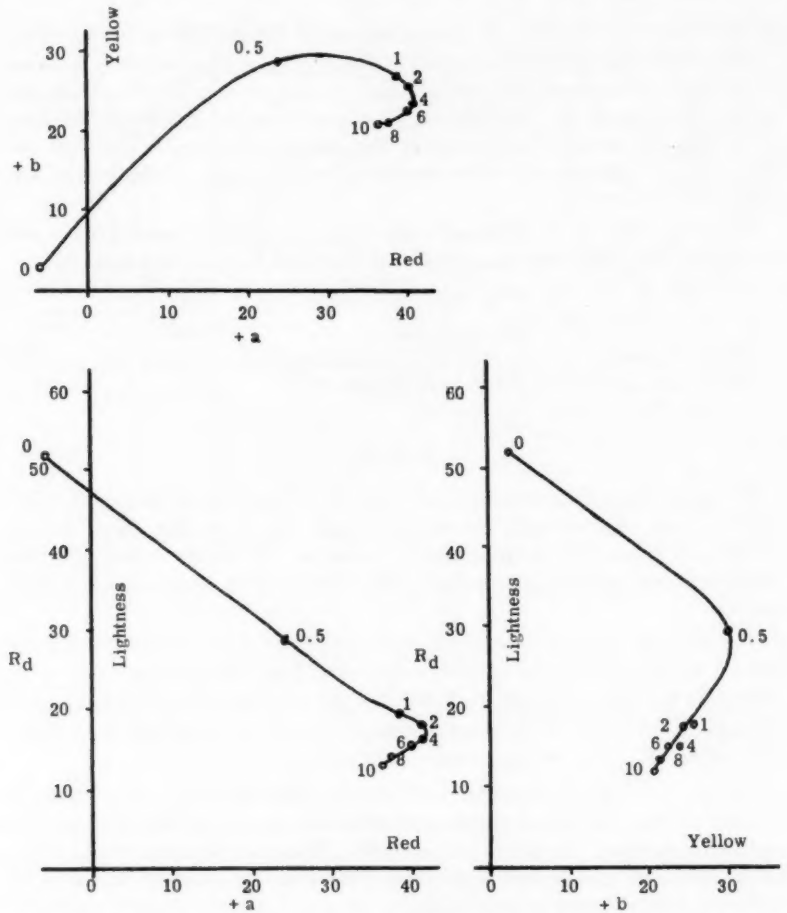


FIGURE 3.—The same dye locus as in Fig. 2, represented by a plan view ($a - b$ diagram) and two side views ($Rd - a$ and $Rd - b$ diagrams. The numbers next to each point denote ounces of dye per 100 sq. ft. of leather used.

textile materials. It must be concluded that the characteristic change in color with increasing dye levels is common to all dyeing processes.

Coloring Efficiency

Another peculiarity of the dye locus is that as the dye level is raised the color at first changes considerably but soon becomes nearly constant. This may be seen on Figure 3 where the numbers opposite each color point refer

to the amount of dye used, in terms of ounces of dye per 100 sq. ft. of leather.

Apart from the gradual closing-up of the color points—a property common to all dyes—it is found that the absolute spacing of points differs from dye to dye (see Figure 4). This spacing of points along the dye locus (for a set of definite dye levels) is a function of the coloring efficiency of the dye, i. e. the inverse of the amount of dye needed to produce a given color on the surface.

The colors that can be obtained when using a given dye, type of leather and conditions of dyeing may be completely described from a knowledge of:

1. Shape of the dye locus, and
2. The coloring efficiency.

These two items must be considered separately if the effect of any variable on the resulting surface color is to be investigated.

Results

It was felt that dyes actually used in leather dyeing should be used for this investigation. Accordingly, we requested from the major dye supply houses samples of those dyes most commonly used in the leather industry. This study is based on the dyes supplied by the dye companies in response to our request.

The present work is limited to acid and direct dyes applied to chrome tanned leathers, with and without subsequent vegetable mordanting.

Results are presented in the form of dye loci for each series of experimental dyeings. Plan views of the loci are shown, that is, *a-b* diagrams, with lightness values (R_d) written in at appropriate points.

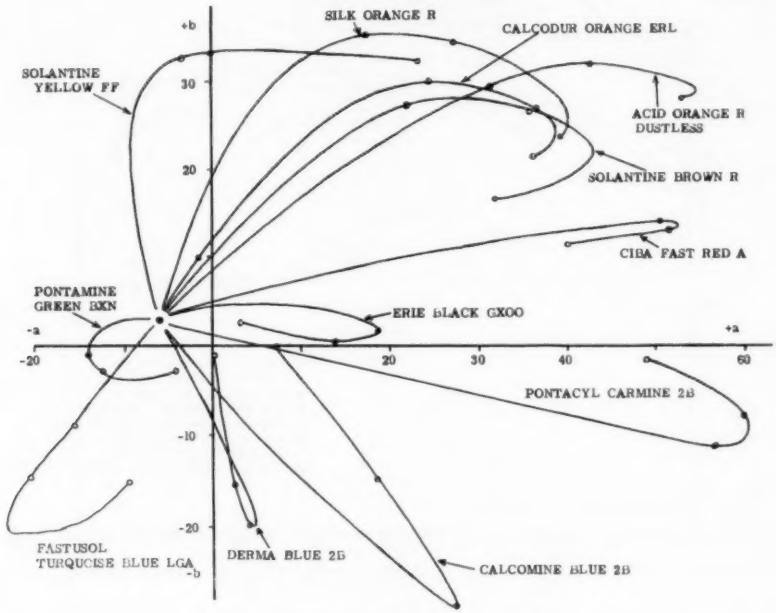
Examples of various dye loci are shown in Figure 4.

Only three color points are shown on each locus, those for ½, 1 and 10 ounces of dye per 100 sq. ft. respectively. The relative positions of these points illustrate the often considerable differences in coloring efficiences of different dyes referred to previously.

Shape of Dye Locus:

The shape of the locus for a given dye remains constant under a wide variety of conditions. In particular, it is unaffected by changes in the pH of the dyebath (provided the dye itself does not change color with pH). Further, the locus remains essentially unchanged on different kinds of chrome tanned leathers. This is illustrated in Figure 5, which shows the locus of Calcodur Orange ERL on eight different leathers.

All the straight chrome tanned leathers (side, calf, kid) have much the same locus. Vegetable mordanted leather on the other hand gives a very



EXAMPLES OF VARIOUS DYE LOCI

FIGURE 4.—The three points on each locus represent dye levels of 1/2, 1 and 10 ounces of dye per 100 sq. ft. of leather. The relative spacing of these points is a measure of the coloring efficiency of each dye.

different locus. The vegetable tanning material itself is colored and therefore it invariably produces darker and less saturated, i. e. duller colors.

The addition of a neutral naphthalenic syntan prior to dyeing has the effect of producing lighter and often more saturated surface colors, as illustrated by the examples in Figure 6.

Coloring Efficiency:

The coloring efficiency is found to be highly variable and apparently sensitive to small changes in the leather, in processing variables, or both. This may be seen by referring to Figure 7 which shows the loci for two dyes, run in duplicate.

In contrast to the nearly constant shape of the locus, the coloring efficiency, as represented by the spacing of points, is very poorly reproducible. This is especially so at low dye levels. At higher dye levels the agreement is better because there, as mentioned previously, the points close up.

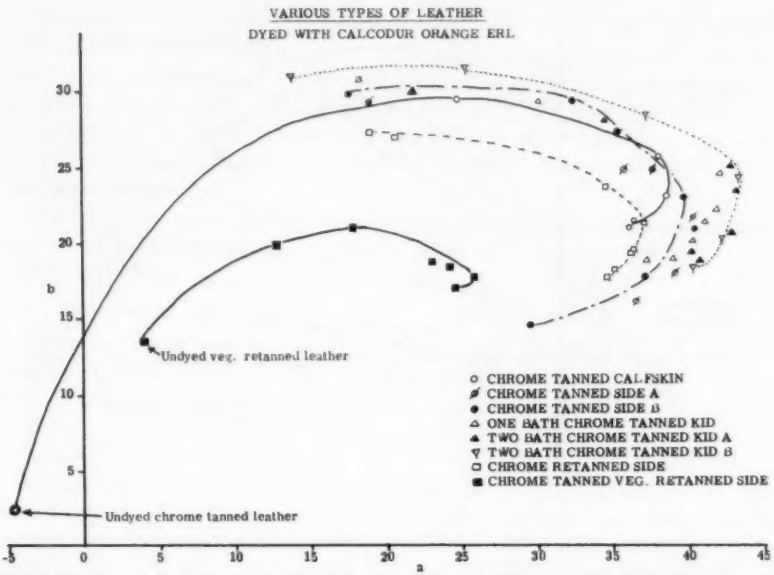
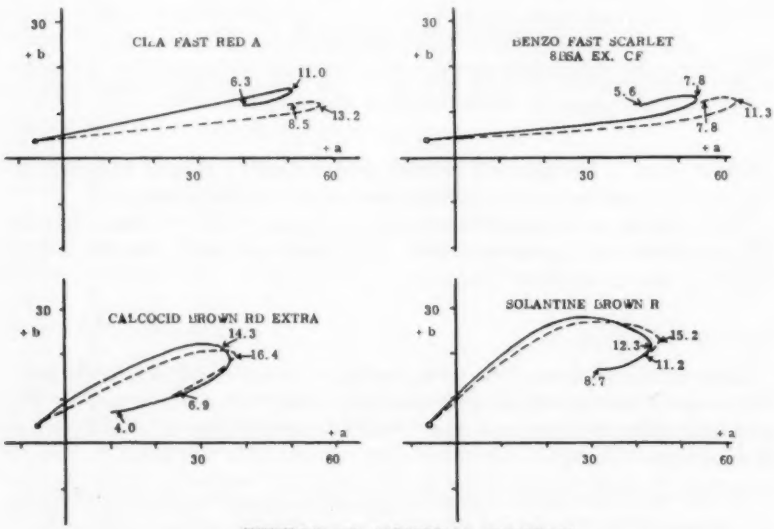
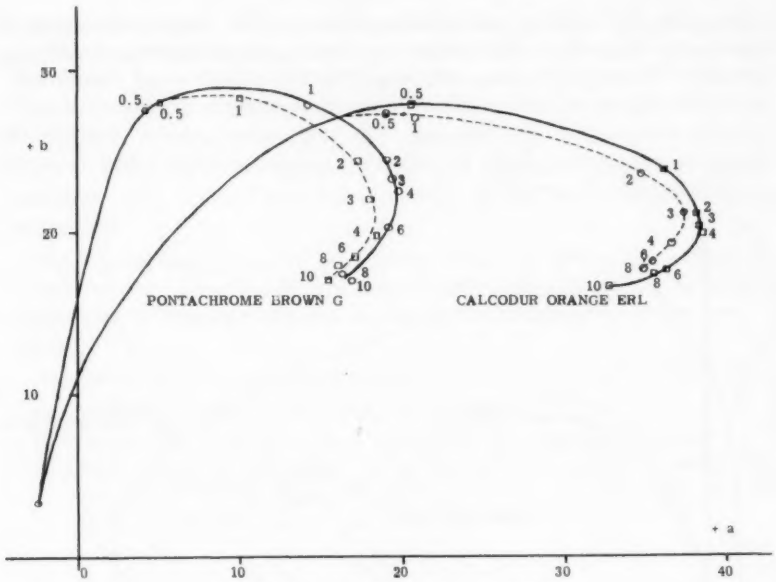


FIGURE 5.—Loci of the same Dye (Calcodur Orange ERL) on various leathers.



EFFECT OF NEUTRAL SYNTAN.

FIGURE 6.—Solid lines—without syntan; Dotted lines—with 1% neutral syntan The numbers represent Rd (lightness) values at the points indicated.



REPRODUCIBILITY OF RESULTS

FIGURE 7.—Duplicate runs show good agreement of locus shape but poor duplication of spacing of corresponding points, i. e. coloring efficiency. The numbers next to each point denote ounces of dye per 100 sq. ft. of leather used.

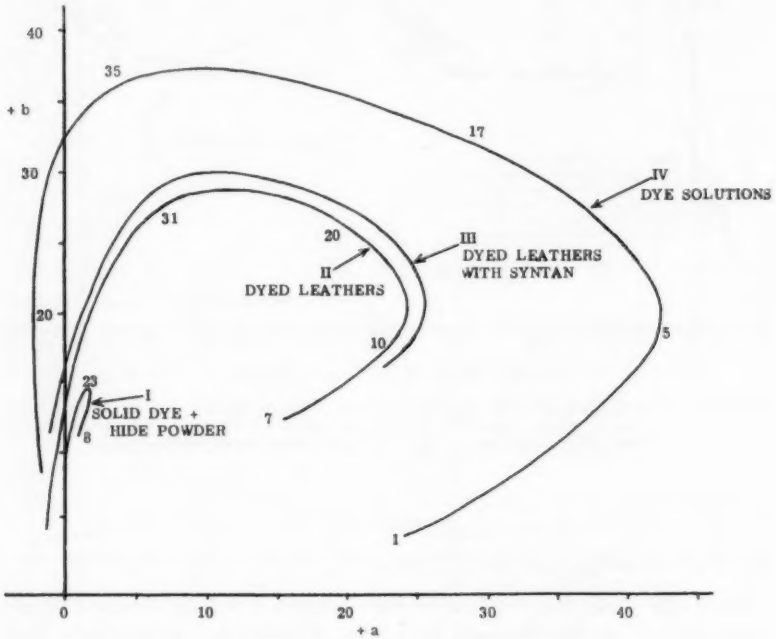
Discussion

The Relative Constancy of the Dye Locus:

When dye is taken up by leather from solution it will be adsorbed on the surface and also in the interior of the leather, if there is any penetration. Only the amount of dye deposited on the outermost, i. e., visible part of the leather will contribute to the resulting surface color. Apart from obvious color changes in the dye itself due to pH effects, or to introduction of other colored material (such as vegetable tannins) the only possible surface color change will be that due to a variation in the amount of dye present on the surface. The dye locus being the range of colors resulting when the amount of dye *only* is varied, one would expect a given dye to give rise to a constant and characteristic dye locus.

Unfortunately the situation is not that simple. It is well known that many dyes in solution exist in the form of micelles, i. e. aggregates, instead of in molecular dispersion [8]. Such dyes may become attached to the leather surface as micelles, and the color then will be different from in the case of molecular

adsorption. The limiting case of dye aggregation is the actual precipitation of the dye on the surface, the surface color then approaching that of solid dye crystals. The other limiting case would be the adsorption of dye in truly molecular dispersion (never realized in practice) with the dye locus approaching that of a range of dye solutions of varying concentrations. Actually the degree of aggregation of the dye adsorbed lies between these two extremes, as illustrated in Figure 8.



EFFECT OF DYE AGGREGATION

FIGURE 8.—Curve I—Locus of dry mixtures of dye crystals and hide powder (100% aggregation)

Curve II—Locus of series of dyed leathers, without additives (normal degree of aggregation).

Curve III—Locus of series of dyed leathers with syntan added (aggregation partly suppressed).

Curve IV—Locus of series of dye solutions of varying concentration (molecular dispersion).

The numbers represent R*d* (lightness) values where placed along the curves.

In this figure the full range from 0 to 100 per cent aggregation is covered, and shows the resulting change in locus.

One would expect, then, the locus to be highly variable, depending on the degree of aggregation. The observed constancy of the locus, in the absence of additives, suggests that in the majority of cases, and for usual dyeing conditions, the degree of aggregation is also constant for a given dye.

Addition of a neutral syntan usually produces lighter and more saturated colors as shown by the experimental results in Figure 6. This effect is represented by curve III in Figure 8 and is shown to lead in the direction of less aggregation.

The syntan occupies active sites on the fiber and thereby slows down the take-up of dye. That this in turn should lead to less aggregation, by causing a more even deposition of the dye, is a satisfactory explanation of the observed effect.

The factors influencing the dye locus may now be summarized as follows:

1. Color change of the dye itself due to pH effects.
2. Introduction of other colored material (e. g. vegetable tannins).
3. Change in degree of aggregation—decreased aggregation by addition of neutral syntan or increased aggregation due to unfavorable pH, too low a temperature, or excessively high dye levels.

Coloring Efficiency:

As was mentioned previously, this second criterion of dye behavior is measured by the inverse of the amount of dye required to produce a given color. The efficiency will therefore depend mainly on the inherent coloring power of the dye. While this is an individual property of each dye it may vary due to changing amounts of diluents (salt, starch, etc.) present.

In addition, the coloring efficiency is also dependent on the degree of penetration. Penetration is of great importance as such and extensively used as a basis of classifying dyes. Apart from this, penetration directly determines the amount of dye left on the surface, for a given amount of total dye take-up.

The degree of penetration is governed by the balance between the rate of diffusion of dye solution into the fiber network on the one hand and the rate of adsorption of dye from the solution onto the fiber on the other hand. The kinetics of this simultaneous diffusion and adsorption have been reviewed by Vickerstaff [1b]. For our present purpose it is sufficient to point out that while the penetration of a given dye is approximately constant, it will be considerably affected by changes in pH, dye concentration in the solution, and presence of any material such as neutral syntan that competes with the dye for reactive fiber sites and thus slows down the rate of adsorption.

In addition, the degree of aggregation discussed above will also influence both rate of diffusion and of adsorption, and thus the degree of penetration.

An indirect effect of penetration, often overlooked, is that some dyes are taken up so strongly and rapidly on the flesh side of the leather that little dye remains to dye the grain surface.

It is seen therefore that coloring efficiency depends, in a highly complex manner, on many variables of the dyeing process some of which are difficult to control. Great difficulty in reproducing coloring efficiencies is to be expected under such circumstances.

The factors responsible for coloring efficiency of a given dye may be classified as follows.

1. Inherent coloring power
2. Degree of penetration. This in turn depends on
   (a) rate of diffusion
   (b) rate of adsorption
   (c) degree of aggregation.

In addition to the color *per se*, as measured by instruments, the effect of texture of the leather surface on visual appearance must be considered. Both the spectrophotometer and the colorimeter measure only diffusely reflected light; gloss is specifically excluded, as stated under color measurement. Gloss however always has some effect on appearance, and especially so where the leather has been glazed, or where a finish has been applied. Two samples, one glazed and the other not glazed, may give the same color values on the machine yet be quite different in appearance. Full standardization of the dyeing process therefore requires an independent measurement of gloss.

Finally it should be remembered that a single color measurement taken over an area of only 1 square inch or less (as is the case with the usual type of instrument) gives no information on levelness of dyeing, a property which can greatly affect the overall appearance. All color measurements should for this reason be checked against visual inspection.

Acknowledgment

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In addition the writers' special thanks are due to Messrs. C. H. Geister, J. W. Pfeiffer and Dr. E. I. Stearns for helpful information at certain stages of this project.

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Received Feb. 21, 1955.

Discussion

Dr. J. Stanley Kirk (General Dyestuff Corporation); Mr. Chairman and Dr. Strauss, I want to congratulate Dr. Strauss on his courage in tackling this extremely simple problem! Most of our work—and we have done a lot of reflectance work—has been done on the Hardy General Electric spectrophotometer. I am sorry my good friend Mr. Davidson is not here. He certainly is far more qualified to discuss this than I. However, there are some things which I want to point out.

I have no quarrel with anything presented but I wish to point out some difficulties which we have encountered.

We still match our leather colors by eye. We run reflectance measurements on our matches whenever we can get at the instrument.

Most leather colors are fairly full colors. They are usually, with the exception of the light tans, in the range of browns, dark browns and even in the blacks. That, unfortunately, is the range in which the reflectance values are of the least value to you. In fact, it is practically useless on the black.

A second point: most of the direct colors which are used are not independent of the sub-strate to which they are applied. Certain of the colors shown there are chrome colors, which chrome partially in the process of dyeing. Therefore, the full shade of the colors are not always developed fully and real values of these colors vary with the time, temperature and amount of free chrome present.

I am speaking primarily from a practical standpoint here now, in the use of colors. Perhaps that is where we might be a little apart. You get full color value at a fairly high temperature. In other words, two of these colors shown on that slide should not be dyed at less than 140 degrees Fahrenheit.

Another point is that most direct colors are associated in solution. Direct colors, as you know, dye neutral, that is, most of them do. They dye through apparently other than primary valence forces. They are associated in solution and therefore are very difficult to measure through transmission measurements, spectrophotometrically. They give you an enhanced color on the surface, because they apparently dye to a certain extent as aggregates.

The acid colors, such as the two oranges shown there, are, as practically all of you know, extremely penetrating colors. They are not surface dyeing colors and consequently give reasonably uniform color regardless of design conditions.

The value of a color is very much of a question how a dyestuff functions. Apparently a dyestuff can coordinate with the chrome nucleus and become part of it in a manner similar to any other organic or sulfonic acid. In fact, it is possible, with one of those colors shown there, according to Otto a good many years ago, to strip chrome from the leather.

Now there is just one other thing. None of us, in leather dyeing, works with one dyestuff. If we do, it is a lucky strike. We usually have two or more.

If you are going to use two or more colors to develop a shade, you are going to run into something else. If the colors are very close spectro-photometrically, your match will be very good on two lights. If they are strongly metameric, no two observers will see that color exactly alike. And I only have to point out to you that regardless of the instrumentation—and incidentally I am not knocking the instrumental evaluation of a color—I am not convinced of some of the things about which we should like to be convinced, on instrumental matching of colors. In fact, I use my eye and the eye of the colorist for ultimate matching.

Now then, to go into those matches which were made and that are strongly metameric, you will have difficulty because not only will they vary with the observer, but they will vary with the light in which they are viewed. So it is the goal and the ambition of a good many of us who are working in this

field, to try to get leather colors, or matches, made for seasoned shades in such way that they have the same hue or approximately the same hue under different illumination. That is shift, no shift, or little shift. That is practically impossible for one fundamental reason. You want colors at a price and because of that it is necessary to make your blends sometimes with widely separated colors.

I do not have any specific questions to ask. I merely wanted to elaborate.

DR. STRAUSS: May I make a few comments:

I would just like to say, in reply to Dr. Kirk, that as far as the chrome content is concerned, it seems to me the chrome level at which one operates in normal practice is low. One can change the maximum amount of dye that can be taken up, but since we operate so far below that level, it seems to me that the chrome content cannot make a great deal of difference.

As far as the metameric color changes are concerned, I realize very well that most instruments, at least instruments depending on filters, cannot distinguish between metameric matches. However, as to the whole concept of the constancy of the dye locus, as I said before, let us think of the locus as a band rather than a line and I think metameric changes would still be within the width of that band. I think that is all I have to say.

MR. CARL H. GEISTER (E. I. du Pont de Nemours and Company): Mr. Chairman and fellow members: Dr. Strauss is to be congratulated for his contribution to a rather controversial subject, but it does give us further understanding of the importance of color. Dr. Strauss readily admits there is additional work indicated, particularly to correlate all the performance idiosyncrasies of individual dyes. Dr. Kirk has covered a lot of these points thoroughly and since the time is getting late, I believe it would be timely to call a halt. If anyone would like to talk over anything specifically, Dr. Strauss will be here and be glad to talk with them on the subject.

The Estimation of Chlorides and Sulfates in Leather

By J. JANY

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The knowledge of the exact amount of chlorides and sulfates contained in chrome or vegetable tanned leather is sometimes of considerable importance, and many methods have been established for this purpose, which can be divided into following three groups:

1. Extraction of the specimen with aqueous solutions of alkalies or alkaline salts. [1], [2]

2. Total destruction of the specimen with nitric acid, with the addition of barium chloride or silver nitrate during or after the destruction. [3], [4]

3. Incineration in the presence of alkalies, generally sodium carbonate. [5]

The serviceability of group (1) is extremely limited. If the leather is vegetable tanned or, if it had mineral tannage but it contains substantial amounts of alkali soluble organic substance, the interference of these materials prevents its application entirely. Even in the case of aniline dyed chrome leather the dyestuff extracted makes titrations with silver nitrate impossible, causes gray colouration of silver chloride precipitates by reducing silver nitrate to metal, and barium sulfate precipitates suffer dirty discolorations which don't disappear even by strongest ignition. Therefore the method can be considered absolutely reliable only if applied to straight chrome leather, undyed and un-retanned.

Methods belonging to group (2) are based upon the erroneous assumption that liquefaction of the specimen means destruction of the organic substance present. It is true that complete liquefaction can be obtained in most cases, but the solution is full of hydrolised organic products which exert their interference in all determinations. Therefore all these methods should be rejected finally.

The third group should be preferred to the other two, because it warrants full destruction of all organic substance. Although its application has been suggested for determination of free acid only, it could be found that the total amount of chlorides and sulfates can be estimated easily by this way, after some adjustments were made in order to increase its accuracy and safety. The reasons of these adjustments will be explained in the description.

Following modification of the method has been found most serviceable:

Ingredients:

10 per cent of sodium carbonate.

12 per cent of glacial acetic acid. Pipette 10 ml. of the sodium carbonate solution and titrate with the 12 per cent acetic acid solution, by adding the latter from a burette. Note the consumption, and in a later stage, when the solution of the specimen has to be neutralised, add the same amount to it. This will be always a little excess, because a minute amount of acidic matter will be produced during the ignition of the leather, but this will be buffered sufficiently by the sodium acetate obtained in neutralisation. Silver chromate being insoluble in weak acetic acid solutions, a small excess has to be considered as harmless anyway.

0.1 normal silver nitrate solution.

10 per cent potassium chromate solution.

Appr. 0.3 normal barium chloride solution.

Conc. hydrochloric acid.

Weigh 5 grams of finely ground leather into a platinum dish. As a rule, low amounts of chlorides and sulfates are contained in the leather only, and therefore 2 grams cannot be considered sufficient. More reliable figures are obtained when increasing the amount to 5 grams.

Wet the specimen thoroughly with about 10 ml. of distilled water, using a short glass rod which is left in the dish. Pipette 10 ml. of the soda ash solution into the dish, and stir well. Heat in an electrically heated air bath under repeated stirring, until the leather disintegrates perfectly into a heavy, homogenous paste. The water bath has been found too slow, because the mass boils above 100°C. After having reached the proper consistency, take the rod out, and rinse all adhering particles into the dish with hot distilled water.

Evaporate to dryness in the same air bath, but at this stage a 250 W infrared bulb may be preferred to the electric heater, because rising and splashing of the heavy mass can be prevented by this way.

Put into an electric furnace, and keep at 400–450°C. for two hours. This temperature is sufficient to char the specimen completely, leaving pure coal, without tar or any kind of soluble organic substance. Higher temperatures should be avoided because of the danger of chloride losses.

The remainder of the ignition is a loose flaky substance which can be transferred easily into a beaker with the aid of a spatula. Boil the dish three consecutive times with distilled water, stirring and rubbing its wall with a short glass rod, and rinsing each time with hot water from a spray bottle. Some dark substance will still adhere to the wall of the dish, but it could be stated definitely that it consists of pure coal and it does not contain any mineral constituents. The dish has been ignited and re-weighed many times after the wash, and in all cases either the original weight or a slight decrease of a few tenths of one mg. was found, none of the checks showed increase. Therefore this remainder cannot have any bearing upon the results of the analysis, and it can be disregarded entirely.

The contents of the beaker are stirred and boiled for 5 minutes or longer if evaporation of excessive water is necessary, and then transferred into a 250 ml. volumetric flask, rinsing with hot water from a spray bottle. Cool the flask, add the necessary amount of acetic acid, fill up to the mark, and filter through Whatman 42 paper. Clear and water white filtrates were obtained in all cases, no matter by what way the leather has been tanned and finished.

Only if the leather contained chrome, did it occur sometimes that the filtrate had a faint greenish yellow coloration which was however hardly appreciable. This can be eliminated easily by adding one gram of zinc powder to the beaker before boiling starts; all soluble chrome is reduced and precipitated by this way. Other reducing agents, like different modifications of zinc, Devarda's alloy and aluminum metal were found unsatisfactory in

alkaline solutions. The zinc powder filters off easily together with the coal, and does not cause any trouble in the analysis, except a minor influence upon the volume of the solution. This influence is negligable, considering that zinc powder loses its bulk in contact with water, the air between the particles being replaced by water, and its volume will be about 1/7 ml. only, as its true specific gravity is 7.14.

Although the volume of carbon, and—if zinc was added—also of zinc has some influence upon the volume of the liquid, this influence is of minor order, and the method described had to be chosen as most convenient. It is impossible to eliminate all carbon by ignition, even if higher temperatures are chosen, because of the presence of soda ash. This is why the A.L.C.A. Methods specify repeated ignition after filtration, a really cumbersome procedure. On the other hand the solution could be filtered after boiling in the beaker, and the filtrate collected and filled up in the volumetric flask. However, the coal being rather retentive, high amounts of distilled water and long washing would be needed to take out all soluble matter, which makes the procedure rather awkward. Therefore, preference has been given to the above described manipulation, i. e. to transfer solid and liquid contents of the beaker to the volumetric flask, fill up to the mark, and filter afterwards.

After filtration, titrate 100 ml. of the filtrate with 0.1 normal silver nitrate, using potassium chromate as indicator.

Pipette another 100 ml. into a 400 beaker, dilute with water, acidify with hydrochloric acid, precipitate hot with barium chloride, and weigh as barium sulfate.

Calculation:

$$\text{Per cent Cl} = 0.177285 \times \text{ml. } 0.1\ N.\ AgNO_3$$
$$\text{Per cent } SO_4 = 20.5765 \times \text{grams } BaSO_4$$

Summary

A method for estimation of chlorides and sulfates in leather has been described, based upon destruction of all organic matter by charring in the presence of sodium carbonate, at low temperature.

Reference

1. Methods of Sampling and Analysis, A.L.C.A., D 20.
2. Ibid. D 21.
3. Leather Chemists' Pocket-Book, H. R. Procter, pp. 191-2.
4. VAGDA Kalender, p 175.
5. Methods of Sampling and Analysis, A.L.C.A., B 21

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New Aspects of the Molecular Organization of Collagen

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The results of numerous investigations of the stability and reactivity of collagens (the corium of mammalian (bovine) and teleost skin) during the last twenty years [1] as to their implication on our ideas of the nature of the cohesive forces of the collagen structure (cross-links) have naturally been interpreted on the basis of the classical concept of collagen. It is conceived to be made up from straight polypeptide chains, parallelly aligned. With the promulgation of the concept of the helical structure principle [2], the problem of cross-linking was radically altered, presenting entirely new aspects. However, none of the collagen models on the helical principle hitherto suggested have been able to account fully for the known facts of the properties and behavior of collagen established by electron-optical and chemical methods. Nevertheless, it appears that the main evidence at hand supports the idea of the helical configuration of the collagen molecule. Already, at this junction, it should therefore be pointed out that the interpretation of the information on the chemical behavior of collagen in the near future must recognize the entirely different spatial environment encountered in the helix structure. The reverse should also be highly desirable. However, the present discussion will principally be restricted to the prehelical conception of collagen and only in a few instances some suggestions as to the application of data to the helical model will be attempted for the reason mentioned and moreover, since such an extension would be outside the competency of the present author.

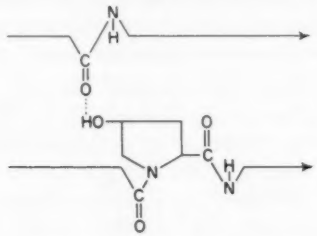
1. *The hydrogen bonding of the hydroxy group and the carbonyl group of the keto-imide linkage.*

The results of recent investigations of the collagens of mammals and teleostei [3] indicate, that the degree of stability of the collagens is directly related to their content of hydroxyproline residues. Thus, the appreciably lower content of hydroxyproline in fishskin collagen than in mammalian collagen appears to be the main reason for the marked difference in hydrothermal stability of the two types of collagen. Measured by the temperature of shrinkage of the collagen, the Ts, the teloest collagen, for instance that of codskin, shrinks at a temperature of 40°, while bovine collagen withstands temperatures up to 65°. The hydroxyproline figure for codskin collagen is about 6 per cent on the weight of the skin, while the value for bovine skin is about 13 per cent [4]. From investigations of the effect of N- and O-acetylation

of bovine collagen [5] upon its reactivity [4], it has been concluded that the hydrothermal stability of bovine collagen in excess of that of the collagen of the bathybic teleosts (equivalent to a temperature range of about 25 °C.) is due to the presence of interchain hydrogen bonds between the hydroxy group of the hydroxyproline residue and the carbonyl group of an adjacent keto-imide linkage [4]. By N-acetylation, the Ts is not altered [4], while by an exhaustive acetylation, inactivating all basic groups (lysine + hydroxylysine) completely and all hydroxy groups except one group out of four hydroxy groups of hydroxyproline, the Ts is lowered from 65 to 40°, or to the point of the Ts of codskin collagen [4]. Thus, the acetylation of the hydroxy groups results in splitting of an *interchain* link. This type of bond, –OH---OC(=HN)– is indicated from the changed reactivity of the O-acetylated collagen [4], as will be shown by the summary in the next paragraph. The presence of this crosslink in bovine collagen should then account for its hydrothermal stability in the temperature range: 40 – 65 °C. The hydroxy group which appears to be masked and nonreactive on the exhaustive acetylation [5] forms possibly the mainstay of the cohesion of collagens generally, irrespective of their origin, in addition to the ordinary type of hydrogen bonds between adjacent keto-imide linkages of the collagen chains [4]. There are numerous findings which indicate that the nonreactive OH-group forms an ester link with an adjacent carboxyl group, the –O . CO– interchain link [6], which problem will be further considered in the following.

From the aforementioned investigations [6] of the effect of the inactivation of the hydroxy groups of collagen on its reactivity, the results from series with condensed vegetable tannins (mimosa) and non-ionic complexes of sulphitochromium sulphates are most instructive. The fixation of these compounds by collagen is appreciably increased by its heat-denaturation, and by its pretreatment with lyotropic agents, indicating that the irreversible fixation of these compounds by collagen involves non-ionic protein groups (hydrogen bonding). The mimosa tannins are mainly fixed by hydrogen bonding of the polyphenolic structures on the carbonyl oxygen of the keto-imide group. The very marked affinity of the condensed tannins for modified polyamides, which contain the –CO . NH– linkage as the principal site of binding, is the crucial proof. It is important to note that the non-ionic chromium complexes are not bound by the polyamides. Hence, they are probably not reacting with the keto-imide linkage of collagen. Accordingly, the increased fixation of these chromium complexes by heat denaturation of collagen and by its pretreatment with lyotropic agents (urea, for example)

cannot be due to the freeing of co-ordination sites on the –CO . NH– linkages. By O–acetylation of collagen, the irreversible binding of mimosa tannins by collagen is greatly increased, from 60 to 95 – 105 per cent, on the basis of protein. On the other hand, the fixation of the non-ionic chromium complexes is markedly impaired by the blocking of the hydroxy groups by acetylation, decreases of the order of 30 per cent being commonly found. These findings, with due regard for other facts which cannot be enumerated here, are in harmony with the view that a part of the hydroxy groups is linked by a hydrogen bond to the keto-imide group, schematically, as:



The rupture of such a bond by heat denaturation, or by the lyotropic pretreatments mentioned, should satisfactorily explain both the increased fixation of vegetable tannins (by the freed –CO . NH– bond) and of the non-ionic chromium complexes (by the freed OH– bond), as well as the effects of the blocking of the hydroxy group, that is, the impaired hydroxy-co-ordination of the chromium compounds, on one hand, and the increased binding of the keto-imide-attached polyphenols, on the other. The large decrease of Ts recorded ($\triangle$Ts $= -25°$ C.) is also explained. In view of the marked affinity of the native collagen for the agents mentioned, it is probable that only a few of the hydroxy and keto-imide groups are participating in this interchain crosslinking.

The following considerations suggest that the hydroxy group involved is mainly furnished by the hydroxyproline residue. In the presence of an aliphatic OH group in intermolecular cross-linking, the teleost collagen should form a more stable structure than the bovine type, since the fish collagen contains more such hydroxy groups than the bovine collagen. In view of the reverse trend of the shrinkage temperature, aliphatic hydroxy groups are not likely to be involved to any great extent.

From the classical concept of collagen structure, the hydroxy-keto-amide hydrogen bond must be interpreted to be an interchain link. On the other hand by application of the helical structure principle of collagen, the difference in hydrothermal stability noted would satisfactorily be accounted for by the presence of an intrachain (intrahelical) crosslink, since the stability of the collagen fibre would be expected to be governed by the strength of the hydro-

gen bonds maintaining the coiling of the collagen molecule. A characteristic feature of the helical structure is its strong tendency to form intrachain hydrogen bonds wherever possible, and the stabilization of the helix by such links is not questioned. In the original collagen model of Pauling and Corey [3], only intrachain hydrogen bonds were postulated; a view criticized by Randall *et al.* [7] In this connection it is also interesting to note, that in Huggins' most recent suggestion of a collagen helix [8], a strong intrachain hydrogen bond of the type suggested by the present author [4] is shown; the hydroxy group of hydroxyproline being located at a distance of 2.9Å from the carbonyl group in the next turn of the helix. The interchain link suggested by the author is compatible with the steric conditions in the present model of the collagen helix (private communications from Professor R. S. Bear).

Professor W. T. Astbury has privately communicated some interesting findings obtained on investigating the protein of the cuticle of the earthworm (*Allolobophora longa*) [9], which on the classification by the wide-angle X-ray diagram should belong to the collagen family (the secreted collagens of Fauré-Fremiet) [10]. According to Singleton, working in Astbury's laboratory, its total nitrogen is only 14.5 per cent, while this figure for ordinary collagens is 18 – 18.5 per cent. Also, the proline and hydroxyproline amount to 3 and 15 per cent of the total nitrogen respectively. In spite of the exceedingly large content of hydroxyproline, this secreted collagen shrinks at 40°C., yielding a solution which does not gel on cooling [9]. However, it is very doubtful whether the secreted collagens are true collagens chemically (See Bear [10]). Probably, they are more akin to stretched gelatin gel, and then the hydroxyproline residue should have no effect on the stability of the protein. Further support of this view is the absence of the cross banded structure of collagens in the cuticle protein [9]. Nevertheless, these interesting facts should be noted in this connection.

From considerations of the steric conditions in the collagen helix and the size of certain crosslinking (tanning) agents, to be given in the following, the formation of intrahelical bonds by these tanning agents appears to be less likely.

2. *The ester link between hydroxy and carboxyl groups.*

The first indication of the presence of an ester link in collagen, which is to be considered, concerns the difference in the alkali binding capacity of collagens and of gelatin (alkali-processed). Collagen as well as gelatin contain 1.25 mg. equiv. of dicarboxylic acids per g. collagen, according to the accepted figures of the amino acid composition [11]. In the native, not alkali treated collagen approximately 0.45 mg. equiv. of these groups are amidated, leaving 0.80 mg. equiv. *free* carboxyl groups per g. collagen [12]. For the depilation of skin, alkali (lime + sodium sulfide) is used. According to the extent of the

liming process, a more or less intensive deamidation takes place, resulting in a shift of the pI from 8 – 9 to 5 – 6[13], and an increase of the number of free carboxyl groups[13]. In the manufacture of ordinary gelatin, the collagen (glue stock) is treated for several weeks in saturated lime solution (pH 12.5) previous to the heat extraction of the gelatin (for a few hours at 60°C.). The deamidation is in most instances practically complete, or nearly so[12, 14]. There are only a few data in the literature on the alkali binding capacity of skin collagen, which has been subjected to different degrees of alkali treatment (liming), as a function of the amide content of the collagen. Bowes and Kenton[12] found that the increase in the alkali binding of collagen due to the freeing of carboxyl groups by deamidation in the pretreatment with sodium hydroxide and calcium hydroxide solutions of final pH values of 13 for two weeks was exactly equal to the decrease in the amide content. Thus, at the final pH of 12 the unlimed native collagen fixed 0.38 mg. equiv. base per g. collagen, containing 0.47 mg. equiv. amide groups. The same collagen treated for 14 days in the aforementioned solution at the final pH of 13.0, subsequently restored to the isoelectric state, combined with 0.63 mg. equiv. NaOH per g. collagen which showed 0.22 mg. equiv. of amide groups[12]. The increase in alkali binding amounts to 0.25 mg. equiv. base per g. collagen which figure checks the figure of the amount of carboxyl groups deamidated.

In unpublished work of the present author on the effect of deamidation on the base binding capacity of collagen, the same trend was found. That the effect of the alkali on collagen is practically entirely confined to the amide groups, as to the splitting products, is proved by the fact that the loss in total nitrogen is only slightly greater than the loss in nitrogen incurred by the deamidation[12, 14]. Thus, on an amount of 0.25 mg. equiv. nitrogen lost per g. collagen by deamidation, the total nitrogen (Kjeldahl) was lowered by 0.29 mg. equiv., a very close agreement in view ofthe difficulty of estimating the amide content accurately. In experiments on the alkali binding capacity of proteins, the greatest final pH value to be considered safe is in the neighborhood of 12.5 since at higher alkalinity secondary reactions set in, and large experimental errors are involved. However, at the final pH value of 12.5 the maximum base binding of collagen is practically attained and the data pertinent in this connection have been so selected.

Additional data[15] from the system: collagen –solution of barium hydroxide (in air free from carbon dioxide) in the range of final pH values: 11.5 – 12.5 bring out the same close interrelationship between the extent of the base binding and the amount of free carboxyl groups of collagen, indirectly estimated by the change in the content of amide groups. The amount of base removed by collagen was obtained in the regular manner by the difference in the alkali concentration of the original solution and the equilibrated solution, obtained on titration. Further, direct estimation of the

barium combined with collagen was performed. The alkali-treated collagen was quickly freed from excess solution by suction filtering. The weight of the resulting collagen was recorded, from which the amount of imbibed solution of the residual barium hydroxyde was obtained, after due correction for the amount of water of hydration (20 per cent of the weight of collagen). The moist barium hydroxide-treated collagen was ashed and the amount of barium fixed estimated as the sulfate, after due correction for the barium contained in the solution inside the collagen. For native collagen of calfskin pelt, an amount of 0.35 mg. equiv. Ba was found, for the skin collagen limed at pH 13 for 5 days the figure was 0.50 mg. equiv. and for the skin treated for 3 weeks in this lime-sulfide solution an amount of 0.54 mg. equiv. Ba per g. collagen was found. The loss in total nitrogen amounted to 0.17 and 0.20 mg. equiv. per g. collagen for the samples of 5 days' and 3 weeks' liming respectively, compared to 0.15 and 0.19 mg. equiv. increase of the base binding. Hence, according to the available information, the effect of alkali on collagen on its pretreatment, as far as the carboxylic groups are concerned, is restricted to the partial deamidation of the asparagine and glutamine side chains [13]. No splitting of cross-links involving carboxyl groups is indicated to have taken place.

Examining the data for the alkali binding of alkali-processed gelatin (in solution) at the final pH value of 12, with due consideration of the amide content of the gelatin specimens, some discrepancy between the difference in the figures of the alkali binding by collagen and gelatin and the difference in the amide content of the two proteins is consistently found. Thus, alkali-processed gelatin, which contained 0.14 mg. equiv. amide groups per g. gelatin, estimated by the method of Shore *et al* [16], bound 0.85 – 0.90 mg. equiv. sodium hydroxide. Compared with native collagen the difference in amide groups amounted to 0.3 mg. equiv., while the difference in base binding was 0.5 – 0.6 mg. equiv. Accordingly, an additional amount of 0.2 – 0.3 mg. equiv. *free* carboxyl groups have been released during the alkali-processing of the collagen in the manufacture of gelatin, apart from the 0.3 mg. equiv. accounted for by the deamidation. Completely deamidated gelatin combines with 0.95 mg. equiv. base, the maximum fixation [17]. It seems reasonable to believe that these additional carboxyl groups are formed by the protolytic cleavage of a strong bond in which the carboxyl group enters as a partner, possible with the hydroxy group, *i. e.*, an ester cross-link. This cross-link should then in part be responsible for the insolubility of collagen in water, in addition to the factor of molecular size.

There are several findings which support the contention of an ester link as the mainstay of the collagen molecule [6]. Thus, in a recent paper, Grassmann *et al.* [18] have produced ample evidence for the presence of an ester-link in procollagen, which, by the way, resembles codfish collagen as to its hydrothermal stability (Ts : 40°). Grassmann isolated the DNP – deriva-

tives of the amino alcohols which were obtained by reducing the carboxyl groups of procollagen with $LiBH_4$. Identical amounts of the amino-alcohols were obtained from native and esterified procollagen. In view of the fact that the reducing agent employed requires esterified carboxyls and does not reduce free carboxyl groups, these findings indicate the carboxyl groups of procollagen to be esterified. The presence of sugars bridging the carboxyl and amino groups, already assumed by Schneider [19], is suggested as an explanation. Moreover, Grassmann considers the formation of an ester bond between the carboxyl and hydroxy groups also.

Further, the fact of collagen being insoluble in concentrated solutions, of lithium bromide, an excellent solvent for silk-fibroin, synthetic polypeptides, and generally for structures stabilized by hydrogen bonds exclusively, is considered by Alexander [20] as evidence for the presence in collagen of a cross-link stronger than the hydrogen bond, probably an ester cross-link [20].

Some peculiaries as to the behaviour of collagen to dyestuffs will also appear less enigmatic if such an ester link is present. Collagen combines with simple acid dyestuffs (anionic) stoichiometrically; the maximum amount fixed corresponding to the equivalent of cationic groups of collagen, first demonstrated by K. H. Meyer and Fikentscher [21] for wool-keratin, and by Felzmann [22] and by Otto [23] for collagen. On the other hand, the uptake of simple basic dyestuffs (cationic) by collagen, for instance that of Safranine O, increases from 0.4 mg. equiv. per g. native collagen, containing 1.0 mg. equiv. free carboxyl groups, to 0.8 mg. equiv. after heating the collagen for one hour in water of 60°C. [24]. Since no deamidation had taken place during the denaturation, neither any severing of keto-imide linkages of collagen [24], it appears that by the extended heat-denaturation carboxyl groups are freed from their compensation in the native state of collagen. It appears probable that the carboxyl groups which are unreactive towards the dyestuff-cations form an ester link with the hydroxy groups of the hydroxyamino acid residues of collagen or have undergone intraresidue condensation. In earlier investigations [25] on the effect of hydrothermal denaturation of bovine collagen, denatured by treatment in water of 70° for one minute, on the fixation of cationic chromium complexes which are exclusively attached to collagen by means of carboxyl ions, it was found that the cationic chrome fixation was independent of the brief hydrothermal pretreatment. In view of the rather mild mode of denaturation employed in these experiments (1 min. compared to 60 min. in the investigation of Veis and Cohen [24]), the instantaneous shrinkage in the very brief treatment evidently does not result in breaking of links in which the carboxyl group is partaking, neither in changes making any inaccessible carboxyl available to the chromium complexes by removing any steric hindrance, for instance.

However, by treatment of collagen in the form of hide powder in water of 70°C. for one hour its irreversible fixation of the cationic chromium com-

plexes from the solution of the 66 per cent acid chromium chloride, $Cr_2(OH)_2Cl_4$, containing 1.0 equivalent Cr per liter, was increased from 7.3 per cent Cr_2O_3 to 11.5 per cent Cr_2O_3, on the basis of collagen. The corresponding figure for the 24 hours-treated hide powder was 14.8 per cent Cr_2O_3 [15]. Hence, the cationic chrome fixation was practically doubled by the prolonged hydrothermal pretreatment in the 24 hours' series. The fixation of the non-cationic sulfitochromium complexes was increased to nearly the same degree by denaturation of collagen in water of 70°C. for one minute and by the prolonged treatment at 70°C. for several hours. The increase amounted to approximately 80 per cent of the amount of chromium fixed by the intact hide powder. Hence, it appears that the rupture of cross-links on non-ionic protein groups takes place during the instantaneous shrinkage mainly. No deamidation of collagen occurred during the heat treatment which solubilized about 60 per cent of the collagen in the 24 hours' series. Since the fixation of the cationic chromium complexes is governed by the carboxyl ions of collagen, these data prove the presence of a large part of the carboxyl groups of the collagen (standard hide powder) in the unreactive form (in a stable cross-link or undergone intraresidue condensation which requires a large amount of energy for the splitting). It is of interest to note, that by heating collagen, in which C-terminal groups are absent, to 68°, Bowes and Moss [26] found aspartic acid as a terminal residue. According to Dr. M. L. Huggins (private communication), it seems probable that some groups found in collagen hydrolysis products are not present in the native molecule itself because of intramolecular condensations, which are reversed when the substance is hydrolyzed. For example, the glutamic acid residues may have undergone intraresidue condensation giving a 5-membered ring which includes the nitrogen of the same residue as a ring atom. This residue would presumably be in the R'' location of Huggin's recent collagen model [8], like proline and hydroxyproline. This suggestion will be the object of further experimental tests on the nature and general reactivity of the specimens of heat-treated collagen discussed.

By instantaneous shrinkage of collagen, no increase in the fixation of cationic chromium (carboxyl ions of collagen) is incurred as mentioned earlier [25]. Neither does pretreatment of collagen in concentrated solutions of lyotropic agents change the reactivity of the carboxylic groups of collagen towards the cationic chromium complexes [27]. By prolonged treatment of collagen in solutions of acids and alkalis at final pH values of 1 and 12 respectively, some increase in the chrome fixation is noted which is accounted for by the deamidation occurring, resulting in an increase of the free carboxyl groups [25]. It should be noted that the fixation of agents which react with collagen by means of non-ionic forces (hydrogen bonding) is tremendously increased by instantaneous heat-denaturation of collagen [25] and by the pretreatment with lyotropic and swelling agents (acids and alkalis) [27]. These deepgoing changes

in the reactivity of collagen caused by prolonged heat treatment, resulting in liberation of carboxyl ions from their state of inactivation, probably is one of the main reactions in the making of gelatin *i. e.*, in the heat-extraction of the alkali-processed gelatin, at pH values 7 - 8, advantageously used in practice.

3. *Crosslinking involving the guanidyl residue*

The two aforementioned types of cross-links, apart from hydrogen bonds between adjacent –CO . NH–linkages and the polar attraction of oppositely charged side chains (electro-valent cross-link; "salt-like" links) should then be characteristic for collagens, while gelatin should lack the –OH—CO– hydrogen bond and the –O · CO–ester link. The gelatinisation of collagen should then be due in part at least to the breaking of these cross-links, in addition to the shortening of the collagen chains by protolytic cleavage of some keto-imide groups. It should be noted that acid-processed gelatin (acid pigskin gelatin, for instance) possesses a base binding capacity which is only slightly greater than that of native collagen [14] with due correction for the amide groups. The formation and properties of the acid-processed gelatin are not conforming with the postulate of splitting of ester links of the –O . CO–type in the collagen molecule being essential for gelatin formation generally. However, the breaking of different kinds of crosslinks during the acid and alkali processing may occur, as Ames [28] suggests in a paper teeming with ideas.

Surveying the alkali binding capacity of collagens, their amide content and the accepted values for the total amount of dicarboxylic amino acids, according to their amino acid composition, the following facts are shown. Native collagen contains 1.25 mg. equiv. dicarboxylic acids per g. collagen, of which 0.80 mg. equiv. carboxyls are free. However, the base binding capacity, amounting to about 0.35 mg. equiv., is less than half the theoretical figure [12]. For alkali-processed gelatin, the corresponding values are of the order 1.25, 1.15 and 0.9. Hence, in the native collagen 0.45 mg. equiv. of carboxyls are not able to react with alkali. The corresponding figure for the gelatin is 0.25 mg. equiv. The difference between the two last mentioned figures (0.2 mg. equiv.) may be assumed to be due to the splitting of an ester bond in the alkali-processing of gelatin. It is of the same order as the number of hydroxy groups in collagen which do not react on acetylation [4, 5]. The latter amount to approximately 0.3 mg. equiv., and accordingly there should be 0.3 mg. equiv. esterified carboxyl groups per g. collagen. However, there are present in gelatin an additional amount of 0.25 mg. equiv. free carboxyl groups per g. protein which do *not* react with alkali at final pH values of 12 – 12.5. This discrepancy has been known for long and is usually explained by the assumption that the discharge of the guanidyl ions by the hydroxyl ions requires such a high degree of alkalinity not obtainable in the ordinary

systems, which do not exceed pH 12.5, for reasons mentioned earlier. The pK value of the arginine residue of collagen is assumed to exceed 14[29]. It goes without saying that the main reaction of the base binding by a protein is the interaction of the OH ions with the cationic protein groups which are discharged, the cations of the alkali being compensated electrostatically by the carboxylic ions of the protein only. Hence, the very strong basic group would require large concentrations of OH ions for their discharge. However, there are several indications in support of the view that the nonreactivity of part of the guanidyl groups is due to the masking of these groups, for instance, by their participation in a strong cross-link, and that it is not a question of the OH-ions being present in an amount insufficient for the discharge of these guanidyl ions.

Some findings indicating some anomalies in the reactivity of the arginine residue will be mentioned. Lichtenstein[30] points out that a part of the guanidyl groups appears not to carry positive charge, and is inert ionically. Further, in tanning of collagen with formaldehyde at pH 12, the guanidyl group binds formaldehyde[31], although the formaldehyde fixed does not increase the hydrothermal stability of the collagen. The arginine group of deaminated collagen fixes formaldehyde in the pH range mentioned without any sign of stabilizing the protein[32]. Hence, neither the crosslinking of the arginine groups nor that of the arginine and lysine groups does take place[32]. In globular proteins, the formation of crosslinks between the side chains mentioned has been proved experimentally in the fundamental researches of Fraenkel-Conrat and Olcott[33]. By the treatment of collagen with hypochlorite, according to Sakaguchi, only about 40 per cent of the arginine residues react and are inactivated. Hence, 0.3 mg. equiv. of guanidyl groups per g. collagen resist this drastic treatment, as first shown by Highberger and Salcedo and by the present author[33a]. On the other hand, the arginine residues of globular proteins are completely destroyed by the Sakaguchi reagent. Accordingly, the arginine residue of collagen differs profoundly from the normal behavior of this residue in globular proteins.

The interesting findings of Grabar and his associates[34] prove that the guanidyl group, and the arginine residue generally, is an important part in the gelatin molecule, and of main importance for its normal behavior. By oxidation of gelatin with hypobromite, the arginine group is destroyed, resulting in a product lacking in gel-forming power. Ultrasonics have a similar effect[35]. Further, by the addition of arginine to a solution of gelatin, its gel-forming property is markedly impaired, the reason probably being the competition set up by the added arginine with the guanidyl group of the gelatin for the group in the gelatin which is its partner in the cross-link[34]. The addition of hydroxyproline to the gelatin solution has only a relatively slight effect on its power of gel-forming, which should exclude the hydroxy group of this residue as the partner in the link[34]. Grabar[34] believes the

carboxyl group to be involved primarily, the hydroxy group in the second place. The base binding capacity of the oxidized gelatin of Grabar has not been investigated apparently. However, it should be expected to reach the theoretical value of the free carboxyl groups deduced from the dicarboxyl-amino acid content and the amide figure, provided that the carboxyl is linked to the guanidyl group.

In the investigation of Bowes and Kenton [36] on the reactivity of deaminated collagen, the base binding capacity was also estimated from the titration curve. By the deamination about 20 per cent of the arginine residues were destroyed, apart from the almost complete removal of the ϵ-amino groups of the lysine residue. The maximum base binding of this deaminated specimen of collagen was about 0.2 mg. equiv. greater than that of the original collagen, while the loss in arginine amounted to 0.2 mg. equiv., all per g. collagen. The partial breaking of the link: guanidyl-carboxyl would give an acceptable explanation. However, there are findings which are contradicting the assumption of the splitting of stable cross-links in the deamination. The hydrothermal stability of collagen is not lowered by deamination. On the contrary, a slight elevation of the T_s results [37], and actually, its conversion into gelatin is made more difficult [42]. The presence of intrachain links of the type suggested would not be in conflict with the trend of the T_s noted. However, the stability of the gelatin molecule is apparently governed by the presence of intact guanidyl groups, which would imply that these are present in an interchain type of link. Another interesting modification of collagen is obtained by its esterification, employing methanol adjusted to pH 1 for the methylation of the carboxyl groups [38]. About 0.2 mg. equiv. of the free carboxyl groups of collagen do not react on esterification [39], [40], while gelatin is completely esterified, although a part of the methoxyl groups of the exhaustively esterified gelatin are rather unstable. By this specific esterification of the carboxyl groups of collagen, the hydrothermal stability is drastically impaired, the T_s being lowered from 65° to 30 – 35° [41]. The breaking of the ester type of cross-links may be involved. Since the reaction of collagen on methylation is very complicated and little known, any further theorization is of little avail. Concluding, it should be pointed out that certain circumstantial evidence suggests the guanidyl group to form a link of marked stability, in both gelatins and collagens.

In the clarifying investigations of Ames [14], [42] on the heat degradation of gelatin and the chemistry of the preparation of gelatin, the point is stressed that in the heat extraction of alkali-processed collagen in the making of gelatin certain stable cross-links, in the first hand the cross-amide linkage, are broken, and that internal re-arrangement of the molecules takes place. The acid- and alkali–processed gelatins are believed to contain three types of cross-links of which two are common to both gelatins, while collagen contains all four types of links. Although the result of Ames' more recent researches [14]

have caused him to revise his postulate, it appears sound in the light of the new experimental material reviewed in this paper, except the cross-amide link concept. Those actively engaged in work on collagen and gelatin certainly will back up his statement that "it may be said with some degree of certainty that salt linkages or hydrogen bonds are too easily broken to account for the transormation of collagen into gelatin".

4. *Some special issues*

As to the effect of an ester cross-link on the stability of collagen to proteinases (trypsin), it should be noted, as shown by Neurath and his associates [43], that ordinary proteinases (trypsin) are able to split ester links. Accordingly, their presence cannot be objected to, from the established fact of the proteolytic degradation of collagen. It appears that the marked difference in proteinase susceptibility of various collagens and gelatin, including the effect of their previous history, should be useful for ascertaining the nature of the various links in the collagen molecule. Some of the complications in the behavior of collagen towards proteinases due to the presence of the prolines, *i. e.*, the –CO . N—linkage formed by their condensation into the polypeptide backbone, have been indicated by the pioneering researches of Max Bergmann [44] and Wo. Grassmann [45] on prolidase and prolinase respectively.

From the classical concept of collagen structure, taking the Astbury model as an example [46], the stabilization of collagen by irreversibly fixed agents, such as the tanning agents, is generally conceived to result from the attachment of the multifunctional molecule or ion of the agent to two or more reactive groups on the adjacent collagen chains, a stable bridge being formed which rivets the chains together [1]. The conclusive evidence for such an interchain cross-linking by tanning agents is easier obtained from systems with water-soluble globular proteins, because the effect of the fixation of the tanning agents on the molecular weight of the protein can then be ascertained. Intermolecular crosslinking should increase the molecular weight. The first conclusive evidence of crosslinking by tanning agents was established by Fraenkel-Conrat and Mecham [47]. They showed that the molecular weight of albumins in moderately concentrated solutions is increased manifold by the addition of small amounts of formaldehyde. Further, Pouradier *et al.* [48] have demonstrated by osmometric and viscosimetric methods that chromium salts increase the molecular weight of gelatin at certain concentrations and pH values. Numerous examples on the effect of tanning agents on the hydrothermal stability, the proteinase resistance and the thermodynamic constants of collagen, which have been claimed as evidence for interchain cross-linking [49], carry more weight by this direct demonstration of crosslinking of globular proteins. Recently, direct evidence for the interchain crosslinking of collagen by formaldehyde has been produced by estimating the molecular

weight of the segment of the polypeptide chain of collagen between points of cross-links from the stress-strain relationship of thermically contracted formaldehyde-tanned collagen by Wiederhorn *et al.*[50]. They found that only about one group out of eight lysine-amino groups fixing formaldehyde functions as the site of an interchain crosslink.

While the hydrothermal stability of collagen generally is greatly improved by its fixation of tanning agents, even to the point of the leather withstanding boiling water (chrome leather), the tensile strength of the fibers is not altered[51]. This has been claimed to imply that the mechanism of tannage is not a cross-linking reaction[52]. However, it has been pointed out that two entirely different phenomena are involved[53]; a view which has received general acceptance recently. The cross-linking is restricted to the protofibrils (polypeptide chains) with distances between reactive groups of some few Ångström units, while the fibers and larger units of the fibre bundles are too widely separated to be bridged by molecules with an effective valency span limited to some ten Ångström units.

The hydrothermal stability of collagen is the problem of maintaining the close parallel alignment of polypeptide chains. This is effected in tanning by the introduction of stable bridges between the chains. The tensile strength and other mechanical properties of the fibres and fibre bundles concern other forces, particularly the surface friction of the fibres as pointed out by Speakman[54], as to the behavior of wool.

In view of the forementioned findings, and moreover considering the large size of the molecules of some important tanning agents, it appears less likely that the tanning effect is due to the formation of crosslinks by the tanning agent between adjacent sites in the same helix. From his fundamental electron-optical researches on collagen, Bear[55] concludes that the bulky side chains, such as those of the dicarboxylic acids and the ionic basic residues are present in the band region of the protofibril while the smaller non-ionic groups, and the prolines are preferentially located to interbands. The protofibrils of collagen are aligned corresponding to these chemical features of the regions, normal to the fibril axis (cross striation). This transverse matching of bands and interband has been demonstrated both by electromicrographs and the small-angle X-ray diffraction diagrams. Bear's concept, which is attractive from the chemical point of view, has recently received strong experimental support by Zahn's[56] isolation of the dinitrodiphenysulfone-*bis*-lysine derivatives by hydrolysis of collagen which had been treated with the bifunctional sulfone, that actually is a double-working Sanger reagent. This important finding constitutes evidence for the close proximity of ϵ-amino groups of the lysine residues in adjacent protofibrils. The crosslinking is likely of the interchain type, since the sulphone employed is an excellent tanning agent, increasing the T*s* some 20°. In this instance it is difficult to conceive how such a large bridge ($\sim$ 20 Å) could be accomodated

between two amino groups in the same helix. The researches in Pauling's laboratory, by Schroeder and his group [5-7], on the composition of the dipeptides and simpler polypeptides in partial hydrolysates of gelatin and collagen indicate that the collagen pattern may contain the following amino acid sequence frequently: glycine-proline-hydroxyproline-glycine, which is in agreement with Bear's suggestion of the band-interband distribution of the amino acid residues in collagen.

SUMMARY

From considerations of the behavior of collagens and gelatin in the native and modified states to various agents, and of the titration curves, it is suggested that besides the cross-links between keto-imide groups (hydrogen bonds) and salt-like links joining adjacent polypeptide chains, conventionally acccepted, the collagens contain two additional types of crosslinks, effecting the stabilization of collagen.

1. In mammalian collagen, hydrogen bonding of the hydroxy group of hydroxy-amino acid residues (probably hydroxyproline mainly) with the carbonyl group of a keto-imide group on an adjacent chain is indicated. This is indicated to be an *intermolecular* link. It is considered to be responsible for the hydrothermal stability of mammalian collagen in the range 40 to 65°C mainly (the range exceeding the shrinkage temperature of teleost collagen). This link is not present in teleost collagen to any appreciable extent.

2. In teleost collagen as well as in mammalian collagen, and probably in collagens generally, irrespective of their origin and previous history, an ester-like bond is made probable by numerous circumstantial evidence. This link is probably formed between the hydroxy group which resists acetylation, and the carboxyl group, yielding an –O . CO– interchain crosslink. The main experimental support for an ester bond in collagens is the lower base binding capacity of collagens compared to alkali-processed gelatin: the latter binding about 0.3 mg. equiv. more base per g. protein than collagen, correcting for the different content of amide groups. This amount corresponds to the equivalent of masked hydroxy groups. The ester-link is apparently split in the heat extraction of alkali-processed gelatin, resulting in the liberation of the carboxyl groups partaking in the ester crosslink. This link is considered to form the mainstay of the stability of collagens generally. Its presence in procollagen has been indicated also. By prolonged treatment of collagen in 70° water for a few hours, the content of reactive carboxyl ions is doubled, indicating the liberation of carboxyl groups from their internal linkage, evaluated by the fixation of cationic chromium complexes.

3. It appears that these two types of cross-links are broken on the transformation of collagen into gelatin, and hence that they do not contribute materially to the stability of the gelatin molecule. This conversion is not

simply the breaking of hydrogen bonds and salt-like cross-links. The third type of stabilizing link, supposed to be present in collagens as well as in ordinary non-degraded gelatins is assumed to involve the guanidyl group, probably associated with the carboxyl group to a stable link, resulting in the withdrawal of the carboxyl group (0.2 – 0.3 mg. equiv. per g. protein) from the ionic equilibrium. This masking of a part of the carboxyl groups would account for the discrepancy between the actual base binding capacity of gelatin and the theoretical value, derived from the content of dicarboxylic amino acids and amide groups. The governing importance of the arginine residue for the normal behavior of gelatin, demonstrated by Grabar, supports this contention. Further, the peculiar behavior of some of the guanidyl groups towards certain tanning agents, such as formaldehyde, conforms with the suggestion of the partial masking of the arginine residue in collagen.

4. The concept of tanning agents forming interchain cross-links with collagen is reviewed and experimental evidence for their formation exemplified. It is concluded that the same type of cross-links are probably formed between adjacent helixes of collagen. The formation of intrahelical crosslinks by long-chain and bulky tanning agents appears less likely for reasons of spatial accomodation. The band—interband concept of Bear for the distribution of the two main types of amino acid residues in collagen is discussed, including some recent findings supporting Bear's hypothesis.

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Metal Chelate Tanning Agents

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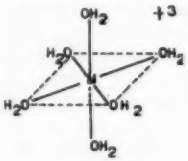
Recent literature on coordination complexes of chromium ion with simple organic acids is replete with theory and practical applications but in the case of dicarboxylic acids only theoretical interpretations are given. Amino carboxylic acids are new and have been proposed as masking agents [1] though no work has been reported nor has the chemistry of chelation been applied to their reactions with the hexacovalent chromium ion and collagen. Recent work by Ackermann and Schwarzenbach [2] treats the kinetics of complex formation and stability of the complexes formed with chromium (III) and ethylenediaminetetraacetic acid (EDTA). Hamm [3] has reported on the kinetics of each functional group of EDTA with chromium (III) and identified the final structure of the complex formed. Although extensive studies of EDTA have been reported, little has been reported on the more simple amino carboxylic acids, especially with respect to hexacovalent chromium ion.

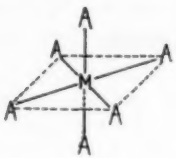
The work reported in this paper covers the effects of the structure of the amino acid or ligand on the masking of the chromium complex, the mode of tannage and on the fixation of chromium by collagen. The method of metal chelate tannage will be described in the second part of this paper.

Our investigation involves the hydrated metal ion of chromium and the discussion will be confined to its trivalent ionic state in solution. In order to visualize how the hydrated metal ion may be changed by complex formation, we wish to represent the hydrated metal ion surrounded by a sheath of water molecules as in Formula 1.

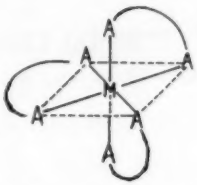


I

The simple complexes are formed through the coordination of the metal ion and a neutral ligand as structurally illustrated in Formula II. A ligand is any complex forming compound. When two or more A donor groups are tied together and bound to a metal ion in a ring structure the complex is said to be a metal chelate compound, Formula III.



II Octahedral Metal Complex



III Octahedral with bidentate ligand

When chelating agents possess two, three, four, five and six donor groups they are classed as bidentate, tridentate, tetradentate, pentadentate and hexadentate, respectively. Thus, chromium having a coordination number of 6 requires three bidentate donors, two tridentate donors or one hexadentate donor.

Thus, the halogens, which act as donors only in the form of their negative ions, cannot form chelates. Similarly, H_2O and NH_3, important complex formers cannot form a chelate ring. The most commonly found organic compounds which form chelate complexes are those in which the electron donor elements are O, N and S atoms. The most common functional groups of organic chelating agents are carboxyl, amino and hydroxyl. Their relative positions determine both the ability of the ligand to form chelates and the stability of the resulting compound. Diehl's [4] classification of chelating compounds considers the total number of "acidic" and "cordinating" donor

groups in order to distinguish between the partial ionic and covalent character of the bonds of any chelate complex.

The commercially successful compounds forming stable chelates with chromium or other metal ions contain both acidic and coordinating donor groups. Amino carboxylic acids, for example, contain acidic carboxyl groups and one or more basic nigrogen atoms as the coordinating group. The simplest amino acid is glycine.

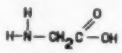


FIG. 1

Glycine, the simplest amino acid, forms chelates with heavy metal ions but not with alkaline earth metal ions. The Log K values for a number of the metal chelates have been reported by Chaberek, Courtney and Martell [5], in a paper discussing glycine and hydroxyethyl derivatives of glycine.

By representing the metal ion in a chelate ring by the letter M the following illustrations show the formation of five and six-membered ring structures. Simple glycine gives a chelate containing one five-membered ring with a metal ion.

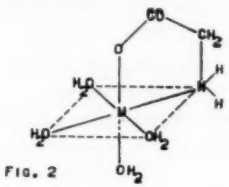


FIG. 2

By substitution of another acetate group forming iminodiacetic acid, two five-membered rings are formed with the metal ion.

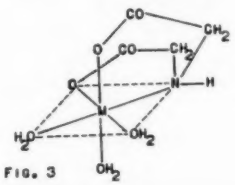


FIG. 3

The nitrilotriacetic acid derivative of glycine results in three five-membered rings.

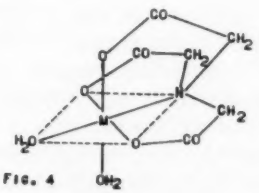


FIG. 4

Extensive work on chelation of metal ions is now well known for the polyaminocarboxylic acid known as ethylenediaminetetraacetic acid, EDTA. This organic compound has the structural configuration,

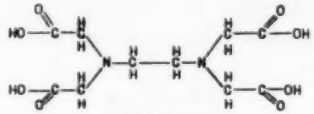


FIG. 5

which contains six donor groupings. It is classed, therefore, as a hexadentate chelating agent. It forms either 4 or 5 five-membered rings with a metal ion. This increase in the number of rings within a particular chelate structure results in greater stability of the chelate. The metal chelates of EDTA have greater stability than those of nitrilotriacetic acid (NTA) or other glycine derivatives.

The reaction between the hydrated chromium ion and EDTA is rather slow and requires heat for more rapid formation. Hamm [3] reports the kinetics of formation with each functional group of EDTA. The subsequent reactions of the acidic donor groups of EDTA proceed in a series of slow steps to equilibrium. At equilibrium, five coordinate positions of the hexacovalent Cr (III) are occupied by EDTA or the displacement of five "aquo" groups by five of the six donor groups of EDTA has occurred as shown.

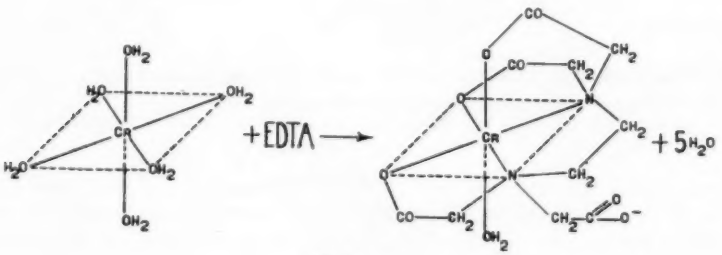


FIG. 6

The chrome chelate of EDTA was applied to washed bated stock and the pH gradually lowered to 4.0 – 4.5. No fixation occurred since washing the treated stock removed the purple-blue complex. This shows that the stability of the chelate complex is greater than that of the chromium-collagen complex. It is apparent that the donor groups of collagen could not displace the chelate rings of the EDTA chromium complex.

Since nitrilotriacetic acid was not commercially available, β-hydroxyethyliminodiacetic acid was used and the tanning value of the chromium chelate of this acid was investigated. The equivalent of 2 per cent Cr_2O_3 (based on limed weight) of this chelate was applied to washed bated stock with

gradually lowering of the pH to 4.0 – 4.5. Fixation of chromium occurred and Table I shows the extent of this fixation.

Table I

β-Hydroxyethyliminodiacetic Acid
Chrome Chelate

Shrink Temp. °F.	% Cr_2O_3 / H. S.
196	4.08

The next chelating agent investigated was bis(N-hydroxyethyl) glycine*. When equal moles of bis(N-hydroxyethyl) glycine and chromium were reacted a purple-blue complex formed slowly on heating. Chromic chloride was used to supply the chromium ion. The chrome chelate solution was applied to washed, bated stock and the equivalent of 2 per cent Cr_2O_3 (based on limed weight) was used. Table II shows the degree of fixation of Cr_2O_3.

Table II

Bis(N-hydroxyethyl)glycine
Chrome Chelate

Shrink Temp. °F.	% Cr_2O_3 / H. S.
210	6.47

The chromic chloride - bis(N-hydroxyethyl)glycine complex proved very successful and the physical properties of the finished leather were satisfactory. A discussion of the various tanning trials and results obtained will appear in Part II of this paper.

It is best, at this point, to note the structure of the chromium chelates of the various polyaminocarboxylic acids to show why the more simple amino acids are the better tanning agents. With EDTA, five coordinating positions on the hydrated chrome ion are occupied and the stable configuration Figure 6, precludes combination with collagen. The relative stability of the EDTA chrome chelate is greater than that of chrome-collagen so displacement of the ligand does not occur.

Nitrilotricarboxylic acid (NTA), forms a very stable tetradentate structure with hexacovalent Cr ion as follows:

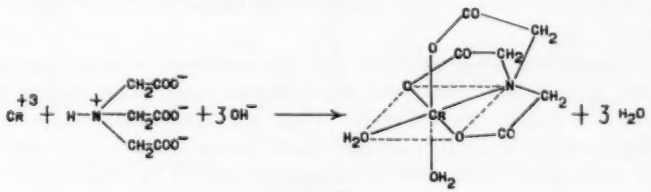


FIG. 7

or $Cr^{+3} + H_3A + 3\ OH \longrightarrow CrA + 3\ H_2O$

*Made by Versenes Incorporated and commercially available as VERSENE Fe—3 SPECIFIC

according to the reaction, three moles of base per mole of metal ion would be required for each mole of chelate formed. Martell and Calvin [6] discuss the titration of NTA with KOH in the presence of metal ions and reactions given on Cr $+^3$, in this case the normal chelate Figure 7, would indicate four coordinating positions occupied. This tetradentate structure should also preclude fixation of Cr by Collagen since the three carboxyl groups are less likely to be displaced by the same groups of collagen.

The next tried was β-hydroxyethyliminodiacetic acid and though some fixation of Cr by collagen was established, the physical evidence points to some blocking of Cr fixation. With β-hydroxyethyliminodiacetic acid there is one less carboxyl group than in nitrilotriacetic acid, thus one less blocking group. In its place is a hydroxyethyl group and from investigations of Chaberek, Courtney and Martell [7], it has been shown that the hydroxyl oxygen has much less affinity for metal ions than a carboxylate oxygen though it does take part in chelate formation. The reaction of β-hydroxyethyliminodiacetic acid with Cr $+^3$ ion becomes:

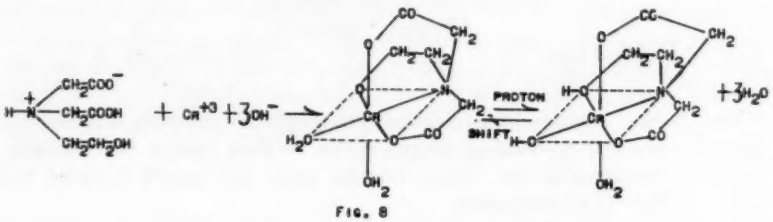


FIG. 8

or $H_2A(OH) + Cr^{+3} + 30H \longrightarrow CrAO + 3\ H_2O$

The tautomeric behavior (proton shift) of metal chelates containing OH groups is discussed under bis(hydroxyethyl)glycine.

It appears that the chromium fixation observed resulted from the availability of an additional coordinating position on the hydrated Cr ion by virtue of the ability of a carboxylate oxygen to displace a hydroxyl oxygen from the coordinated sphere of the metal ion. In this case, the carboxylate oxygen of collagen displaces the hydroxyl oxygen of the ligand from the chrome chelate complex.

It becomes increasingly evident that the extent of coordination and type of acidic groups associated with the hydrated chrome ion determines the extent of Cr fixation by collagen. Thus, the elimination of one or more blocking groups; the acidic carboxyl donor groups, from a given amino carboxylic acid should then result in increased fixed Cr by collagen. This was actually the evidence obtained when bis(hydroxyethyl) glycine was used to form the metal chelate tanning agent. It is also common knowledge that when a simple organic acid, such as, formic or acetic, is used in a mole ratio

greater than 1:1 of acid to Cr that fixation of Cr by collagen is adversely affected. The fixation of Cr by collagen can then be blocked by either a simple complex or a chelate complex providing, of course, the substitute donor groups are acidic carboxyl groups or ionically bound to the Cr^{+3} ion.

In the case of bis(hydroxyethyl) glycine two blocking groups (acetate) on the amino group have been replaced by two hydroxyethyl groups. This means that in the reaction with hexacovalent chromium ion we have the tetradentate structure but four coordinating positions are available to the donor groups of collagen. Another explanation for the ease of fixation of the chrome chelate of bis(hydroxyethyl)glycine by collagen is offered by Chaberek, Courtney and Martell [5] in their discussion of the chelate structure of Fe^{+3} ion and bis(hydroxyethyl)glycine. The hydrolysis of the 1:1 chelate, Figure 9, may involve dissociation of a proton from the hydroxyethyl group or from the coordinated water molecule. Thus, there is the possibility of tautomerism involving proton shifts from the coordinated "aquo" groups to the negative alkoxide groups attached to the metal ion. It is evident that combination of the chrome chelate may involve the displacement of a coordinated "aquo" molecule, the negative alkoxide group or the ethanolic group of the ligand. It is a matter of conjecture to state which does occur in the highly buffered medium of the chrome chelate liquor. However, a drop in pH is always observed which is indicative of the dissociation of protons.

When bis(hydroxyethyl)glycine is added to $^1/_3$ basic chromium chloride solution on a mole per mole of metal ion basis a drop in pH of the solution is observed. Thus, if the amino acid is represented by the Formula $HA(OH)_2$, the reactions are

$$HA(OH)_2 + Cr\,OH\,Cl_2 \longrightarrow Cr\,AO_2 + H_2O + 2\,H^+ + 2\,Cl^+$$

upon addition of two moles of base

$$Cr\,AO_2 + 2H^+ + 2\,OH^+ \longrightarrow \underset{\text{Neutral chelate}}{Cr\,AO_2} + 2\,H_2O$$

The chelate structure of hexacovalent chromium ion is illustrated as

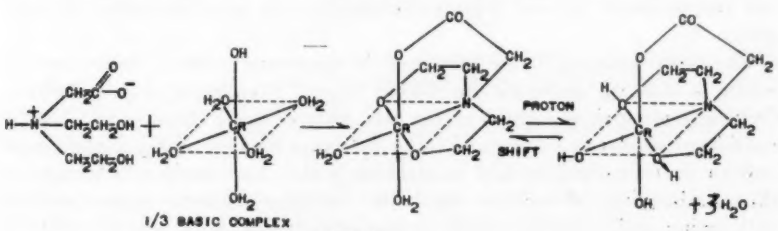


FIG. 9

In this reaction the 1:1 chelate forms with the displacement of the proton from the amino group of the chelating agent which reacts with the hydroxyl

groups of the $^1/_3$ basic complex to form a mole of water. The hydroxyethyl groups are involved in coordination with the dissociation of two protons which accounts for the drop in pH of the solution. Thus, three moles of hydrogen ions are neutralized per mole of amino acid on reaction with Cr^{+3} ion to form a neutral chelate. It is possible to visualize that the probable union of the neutral chelate with collagen is by the formation of a double chelate as shown.

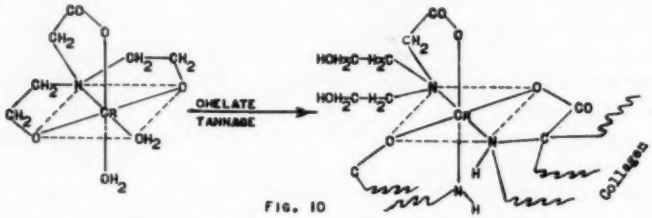


FIG. 10

Chelate tannage illustrated shows that the chromium aquo ion is more completely saturated by donor groups and rendered more stable than the regular fixed basic chrome sulfate complex by collagen. However, the alkoxide groups are free to react with tannins and dyestuffs though the affinity would be much less than that of the negative alkoxide groups on the fixed basic chrome complex of collagen.

Consistent with the mechanism of chelation and fixation of the chrome chelate would be the complex of chromium ion with the simple amino acid, glycine. Glycine has one displaceable proton, hence, it is apparent that it would form a normal 1:1 bidentate chelate with the hydrated chrome ion. Glycine exhibits the tendency to form higher chelates induced by pH changes even on the acid side so any variations in pH of the liquor would alter its masking action. This amino acid would be analogous to the use of formate for masking of chrome liquors but unlike formate a chelate masking. Preliminary tests show that the glycine-chrome chelate tannage is satisfactory but the tendency to form higher chelates has not been thoroughly investigated.

The term "masking" has been used in the sense to show the protective action of masking agents on the chrome "aquo" complex against hydrolysis. Organic acids such as formic, acetic, etc., form simple complexes and can be considered similar to Formula II. The difference between a dicarboxylic acid and an amino carboxylic acid in masking is that both carboxylic groups of the dicarboxylic acid need not react with the same chromium aquo ion while with amino acids a chelate ring is formed on only one metal aquo ion, that is on a mole to mole basis. The chelate ring, then, is the distinguishing feature that differentiates the mode of masking by amino carboxylic acids from simple organic acids or dicarboxylic acids. The exceptions to this rule are oxalic and

succinic acids which form five- and six- membered chelate rings with the chromium ion, respectively.

The experimental work shows that the chelate of bis(hydroxyethyl)glycine more completely satisfies the spatial and coordinating requirements of the collagen donor groups. The double chelate structure is proposed as the mode of fixation of the chrome chelate. It becomes apparent that the stability of the basic chrome-collagen complex is due either to the "salt" linkage or in part to the formation of a ring structure within the individual polypeptide chain. However, the use of a metal chelate ion as a tanning agent permits the same mechanism of fixation of chromium by collagen to occur, while the formation of two or more five- or six-membered rings increases the stability of the fixed chrome.

The use of metal chelates as tanning agents will eliminate the basicity factor; the neutralization process; the need or concern over the two bath processes of chrome tanning and the toxicity of the chromium liquors. The process should improve dyeability of the leather and reduce "crocking" of colors. The process has thrown light on the mechanism of the masking of hydrated chrome complexes and their combination with the functional groups of collagen.

In Part II of this paper we will present all the chemical and physical data covering the "Metal Chelate" process of tanning.

Acknowledgment

The constructive help and criticism of Dr. S. Chaberek, VERSENES INCORPORATED, is gratefully acknowledged. Acknowledgment is also made to Dr. A. E. Frost, VERSENES INCORPORATED, for his criticism in preparation of this paper.

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BOOK NOTICE

The Elements of Chromotography By T. I. Williams. Philosophical Library, Inc., 15 East 40th St., New York, N. Y. 90 pages. 1953. Price $3.75. This book of less than 100 pages offers an easy introduction to chromatography for the chemist who has not had previous acquaintance with the field. While such a short survey is necessarily lacking in the experimental details required for laboratory use, it presents a well-rounded discussion of the various types of chromatographic techniques which have proved so spectacularly successful in the separation of organic and of inorganic substances. After an introductory section on the historical development of chromatography, adsorption chromatography is discussed in a 20 page chapter under the headings of adsorbents, solvents, and apparatus. This is followed by a 15 page discussion of paper chromatography (including inorganic qualitative analysis) and a 7 page chapter on ion-exchange chromatography. Various special aspects, such as reversed-phase chromatography, methods of locating the positions of colorless substances within the chromatogram, displacement analysis, and carrier displacement, are also considered. The book concluded with a chapter on the use of large-scale chromatography in industry. There are few references to the original journal literature, but a sufficient number of books and review articles are cited to satisfy the chemist who wishes to delve further into the method. The paper, printing, and binding are excellent. The book is handsomely illustrated with 7 colored plates.

ABSTRACTS

Industrial Uses of Enzymes. Uses in the Leather Industry. By G. H. Green. *Chem. and Ind.*, No. 4, 84 (1955). Skins, from animals dieing naturally, may be treated with papain to remove coagulated blood, but is too expensive to be justified by the slight improvement gained in leather quality. Pancreatin is the commonest enzyme used in the leather industry. Mixed with deliming ammonium salts it forms the bate of commerce. Bacterial and mold proteases follow in importance in the order named. While synthetic bates are not as effective as dung bates, they are cleaner and less objectionable from the odor standpoint. While pancreatic bates are more effective on swollen skins, the mold and bacterial bates are most suitable for unswollen skins. Proteolytic enzymes can be used for unhairing, the action being similar to the old sweating process. It is first desirable to swell the skins with caustic soda whereby enzyme penetration is greatly facilitated. Enzyme unhairing is especially suitable for goat and some hair sheep skins. Bacterial and mold proteases can be used in the unhairing of unswollen skins. The author does not place much value on laboratory evaluation of bates since no satisfactory substrate has yet been used.

Hycar Resins Open New Fields in the Processing of Leathers. By T. A. Dickinson. *Lea. and Shoes*, **127**, No. 2, 12. (1954). Hycar is used to designate a group of butadiene-acrylonitrile, butadiene-styrene, and polyacrylic elastomers. Butadiene-acrylonitrile copolymers, sometimes referred to as nitrile rubbers, are soluble in nitromethane or nitroethane, ethlene dichloride, chloroform, chlorobenzene or chlorotoluene, acetone, ethyl acetate, and dioxolane. Mineral pigments, softeners and antioxidants can be added. Dispersions containing 10 to 20 per cent of Hycar are suitable for impregnating leather. The solvent can be removed by normal evaporation or hastened by heating the leather to about 150° F. Economy dictates solvent recovery. Hycar materials can be used for surface coatings. If pigments are to be added they are usually separately dispersed with water and wetting agent, and the mixture added to the latex. Typical pigment dispersion mix consists of 100 parts of shellac, 25 parts of borax and 400 parts of water. Hycar adhesives are also suitable for bonding leather to leather when used in conjunction with various resins and casein.

New Methods in Tanning, Dyeing and Finishing of Leathers. By G. Otto. *Lea. and Shoes.* **127,** No. 12. 31 (1954). Fuller chrome leather can be produced by first deliming and bating the skins, placing them in a chrome alum solution, then changing to a 40 per cent basic chrome liquor containing more than the normal amount of chrome. A simpler method is to pickle the skins in sulfophthalic acid without addition of salt. Formates and sulfophthalic acid makes an even better combination. Stock from the chrome liquors is fuller and of finer grain. By the addition of certain cationic soaps to basic aluminum chloride an aluminum tannin (Lutan 0) is formed, which can be added to the chrome liquor with the production of a finer, closer grained leather. When used with spongy skins, this tannage has a tendency to reduce pipey and drawn grain.- To dye uniformly the author recommends reduction of affinity of both hide and chrome, then subsequently raising them. Reduction is effected by the use of neutral salts of a synthetic replacement tannin in combination with neutral salts of aromatic masking acids. The first salts are added to the neutralizing bath, while the second salts are added to the dyeing drum. In fatliquoring chrome leather, it is recommended that the base oil be sulfonated. If the leather is chrome tanned but retanned with vegetable tannin, it is recommended that a sulfonated oil fat liquor be first used, followed by cationic liquor in the same drum.

Separation of Amino Acids on Columns of Sulfonated Polystyrene Resins. By P. N. Campbell, S. Jacobs, T. S. Work and T. R. E. Kressman. *Chem. and Ind.* No. 5 116 (1955). Zeo-Karb 225 ion exchange resins are suitable for quantitative estimation of the amino acid composition of protein hydrolysates. The W. R. (water regain) value of the resin is quite critical, W. R. 2.3 giving incomplete separation of glycine and alanine and slight overlap between phenylalanine and tyrosine whereas W.R. 1.55 resin gives complete resolution of the peaks but rather slow elution of basic amino acids; with W.R. 1.1. resin elution of the basic amino acids becomes tediously slow. The ideal W.R. value for amino acid separation probably lies between 1.55 and 2.3.

Chrome and Zirconium Tannages — A Review and Comparison. I. C. Somerville. *J. Soc. Leather Trades' Chemists,* **38,** 347 (1954). A brief resumé of the history of chrome and zirconium tanning, with its theoretical aspects, is given. In the earlier period of development it was determined that the sulfates were more effective than the basic chlorides or nitrates. A dry salt salt considered to be approximately $Zr(OH)_2 \bullet Na_2SO_4$ was put on the market and has been available as Zircotan N for fourteen years. While not approximating chrome tannage in practical importance, it may be said that zirconium tannage is the greatest advance in mineral tannage since chrome tannage was developed. White leathers produced under tannery conditions with zirconium are: kid, calf, sheep and kangaroo suedes; snuffed side "buck", side splits for suede, waist belt, welting, sole (nurses shoes), sheepskin, skivers, glazed kid, capeskin glove, lace leather, hair-on slunks, and black and white reptile. The use of zirconium with other tanning agents is expanding in the United States. Colored leathers so produced are:- with chrome; kid suede, calf suede, sheep suede (garment) and side upper leather: with vegetable tannage; insole leather, outsole leather and retannage India stock. If the day comes when zirconium salts are in the same price range as chrome, the industry will have a proved alternative tannage which gives stable leather of almost any character desired, but especially one with oustanding plumpness and solidity. There follows a discussion of the chemistry of zirconium tannage with some experimental study comparing it with chrome tannage. Summing it up, it is concluded that under the usual conditions of tanning, zirconium sulfate is essentially in catonic condition. Moreover, when beginning with normal sulfate, some hydrolysis takes place to form basic sulfate which may be taken up by the skin at about 35 per cent basicity, but which is converted to about 75 per cent basicity before completion of tannage. A complete explanation of the mechanism of zir-

conium tannage must be deferred until more is known about the exact composition of the basic sulfate involved and about the fine structure of the hide protein with which combination occurs. R.H.T.

The Deterioration of Pickled Pelts. F. W. Woodroffe and F. G. Caughley. *J. Soc. Leather Trades' Chemists*, **38**, 399 (1954). Complaints concerning the quality of pickled sheep and lamb pelts exported from New Zealand necessitated an investigation of the problem. A study of the deterioration of pickled pelts at the temperatures which might prevail under the conditions of transport was made. The temperatures selected were 7, 20 and 35° C. Analyses of the freshly pickled skins and the same after 12 weeks storage at these temperatures showed that the significant changes from the original condition were in the increase of soluble hide substance and the rise of pH of the water extracts, when stored at 20 and 35°. There was little change at 7°. The following tables give the significant figures.

Soluble Hide Substance as Percentage of Total Hide Substance.

Weeks Storage		0	1	2	4	8	12 Weeks
Temperature	7°C.	2.6	2.4	—	2.3	2.5	2.5
"	20°C.	2.6	—	2.7	3.3	4.3	5.8
"	35°C.	2.6	4.3	5.9	9.2	13.9	17.1

pH of Water Extract.

Weeks Storage		0	1	2	4	8	12 Weeks
Temperature	7°C.	2.14	2.14	—	2.08	2.16	2.17
"	20°C.	2.14	—	2.15	2.14	2.24	2.25
"	35°C.	2.14	2.15	2.22	2.28	2.44	2.52

In view of the deterioration at 20° it was necessary to examine the storage conditions prevailing in New Zealand and overseas, where casks of pickled pelts are held in the open air. The test was made during the months of December, January and February. Average atmospheric temperatures, temperatures 3 inches inside pelts, at the center of pelts and in the interior air gaps (where the pelts pull away from the staves) were recorded. At the end of the period the casks were opened and the pelts examined. Where the pieces had been exposed to the highest temperature, i.e. the air gap, small sections were brown and completely rotten. Apart from this area, it was not possible to differentiate between pieces taken from the middle and those near the outside. A study was made of the effect of sulfuric acid concentrations using the final acid concentrations of 0.1, 0.3, 0.5 and 0.75 percent sulfuric acid, with 15 percent salt in all cases. The experiment is described and data given. It is definitely established that deterioration of the pickled pelt is directly proportional to the free acid present. A finished pickle of 0.8-1.0 percent H_2SO_4 is likely to produce trouble. A modified pickle, finishing with an acid content in the used pickle liquor of 0.3 percent H_2SO_4, results in sounder pelts because of reduced susceptibility to heat damage. Incidence of natural mold took place in 9 out of 68 samples examined. Six showed heavy growth. A study of disinfectants for mold prevention showed that beta naphthol (0.5 percent on the pickle liquor) will prevent harmful mold growth. Heavy mold growth is accompanied by large increases in the pH of the water extract and in the percentage of soluble hide substance. R.H.T.

Theoretical Rules Governing the Co-ordination of Ligands to Chromium. S. G. Shuttleworth. *J. Soc. Leather Trades' Chemists*, **38**, 419 (1954). The ligands of collagen cited in the literature as participating in chrome tannage are, carboxyl groups of the side

chains, the carbonyl groups of the peptide links, the hydroxyl groups of the side chains, the nitrogens of the pepitde links and the amine groups of the side chains. Evidence is given from which the following five rules are deduced. Rule 1. In order to compete successfully with co-ordinate water molecules in an aqueous medium (where water predominates) oxygen atoms must acquire additional electronegativity through a negative charge. A less general but more simple statement of this rule is that acid and hydroxyl groups must be ionised in order to co-ordinate with chromium in aqueous solution. Rule 2. The stability of co-ordination of an acidic group to chromium is inversely proportional to the dissociation constant of the acid. Acidic ligands have been arranged in order of affinity for chromium by many workers including Stiasny, Serfass and Theis, and Cetto, but without separation of mono and polydendate ligands. Rules 2 and 4 combined will be found to fit the findings of these workers. Rule 3. Amine groups do not coordinate appreciably to chromium under aqueous acid conditions, and even under neutral aqueous conditions their chromium co-ordination stability is considerably less than that of carboxyl groups. This rule appears to be a logical extension of rule 1, viz. that the amine groups will have reduced electronegativity because of the positive charge carried under acidic conditions, and will, therefore, show negligible co-ordination affinity for chromium. The removal of the positive charge under alkaline conditions may be expected to increase the co-ordination affinity for chromium. Rule 4. The formation of chelate rings greatly enhances the co-ordination stability. From the evidence and from the bond angle considerations five membered rings are the most stable, six membered rings less so and the seven membered maleato ring still less stable. No evidence could be found of appreciable ring formation of succinates and higher dibasic acid groups. Rule 5. The stability constants of co-ordinated ligands follow a stepwise pattern of decreasing affinity in respect of the six co-ordination bonds of trivalen chromium. The importance of this rule lies in masking phenomena, where the use of organic acids and their salts modifies the affinity of the complex for collagen. The above considerations appear to narrow down chrome tannage to co-ordination with the carboxyl groups only, and make it extremely unlikely that any other groups co-ordinate under aqueous conditions. However other groups might well co-ordinate during the drying and heating of chrome tanned leather. It is important to note that co-ordination implies an entirely different order of attachment to that of either hydrogen bonds or adsorpion forces. It is acknowledged that a part of the chromium may often become attached to collagen by these weaker forces, depending upon the nature of the complex used, but it is believed that this hydrogen bonded or adsorbed chromium plays a minor role in practice. R.H.T.

The Reaction of Non-Cationic Chromium Complexes with Collagen. K. H. Gustavson. *J. Soc. Leather Trades' Chemists*, **39**, 2 (1955). This is an analytical review of the literature of the subject containing some unpublished data. It is summarized as follows. (1) It is shown that, in the fixation of the tetra-oxalato-diolchromiate by collagen, its cationic groups are involved and probably also, secondarily, non-ionic protein groups. Evidence proving the non-participation of the carboxyl groups of collagen is presented. (2) The main part of the sulfito-chromium-sulfates, composed of non-ionic and anionic complexes, are fixed by the non-ionic protein groups. Recent experiments employing collagen, O-acetylated collagen and polyamide, indicate the hydroxy groups of the residues of hydroxy amino acids (hydroxyproline particularly) to be the site for binding of these non-ionic chromium complexes. On prolonged tanning and in the secondary processing generally, the sulfito complexes are gradually decomposed, forming cationic complexes which interact with the carboxyl ions of collagen. (3) Aggregated complexes of non-ionic nature, such as those present in the solutions of basic chromium sulfate complexed with phthalate, and extremely basic chromium perchlorates, react with non-ionic protein groups. These compounds also possess marked affinity for polyamides. (4) In two bath tannage, the main

chrome fixation is cationic, although binding of anionic chromum complexes by collagen through its cationic groups occurs to a minor extent. (5) The effects of secondary reactions in the interactions of the hexa-urea-chromium cation and the anionic hexathiocyanatochromiate complex with collagen are experimentally demonstrated. Mononuclear chromium complexes, which in their original form lower the stability of collagen (hydrotropic agents), are by protolysis in solution or in the fixed state in collagen converted into polynuclear complexes which have stabilizing and tanning effects on collagen. The stability of cationic chrome collagen to 8 M urea solution and the appreciable loss of chromium from some noncationic chromium-collagen-compounds are stressed. Further evidence in support of the view that the mechanism of cationic chrome tannage is crosslinking of adjacent polypeptide chains by polynuclear chromium complexes through the carboxyl ions of collagen (multipoint coordination on chromium) is presented. R.H.T.

Studies in Fellmongering — 1. The Sweating of Sheepskins. G. H. Green. *J. Soc. Leather Trades' Chemists*, **39**, 20 (1955). Previous studies, while contributing much to theory, have been of little practical value. One aim of this investigation is to achieve higher efficiencies and improve both wool and skins. For determining the depilation load (D.L.) the method of Lennox, slightly modified, was used. To minimize the effect of variations, the mean of six D.L. measurements was taken. Checks were made at fellmongeries to determine the actual D.L. on skins from which wool was being pulled. Beam pulling and knee pulling were compared. For knee pulling skins must be sweated to a more advanced state, resulting in a higher incidence of run pelts and a poorer general pelt quality. This and the higher labor cost can only be justified by a higher price for the finer sorting of wool. Eleven strains of aerobic bacteria, present in appreciable numbers, were isolated. Five of these liquified gelatin. Details of morphology and cultural characteristics of the five are given in tabular form. All the gelatin liquefiers were capable of partially loosening wool; but only one, producing ammonia, loosened the wool completely. This ammonia producing bacterium appears to be a member of the genus Pseudomonas but not identical with Ps. putrefaciens. It seems probable that the bacteria responsible for wool loosening are a characteristic of the fellmongery rather than of the skins themselves. During sweating the wool root is partially digested; but there is doubt as to whether bacteria penetrate down the follicle of form the flesh surface. An experiment is described giving results which indicate that the penetration takes place through the flesh surface. During sweating large amounts of carbon dioxide and smaller amounts of volatile acids and ammonia are produced by bacterial action on the skin proteins. In the water in the skin tissues these products are in equilibrium with each other and stabilize the skin pH at about 8.3. Although this pH is somewhat above the optimum for growth of the unhairing bacteria, it is not possible, under normal conditions, to disturb the equilibrium to lower the pH. Ammonia introduced before or during the sweating retards wool loosening, unless added in large quantities towards the end of the sweating, when it completes the loosening as the result of chemical action. Nematodes on the flesh surface of the sweating skins have been found to be beneficial, probably by helping to distribute the bacteria over the skin, and later by keeping down the bacteria population. The source of infestation has been traced to the soak pits and supports in the sweating chambers. R.H.T.

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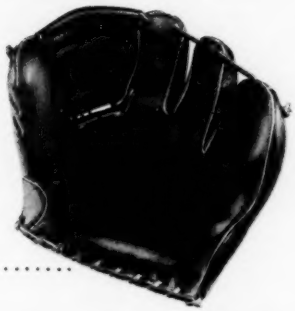

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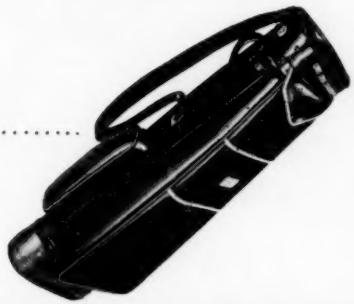

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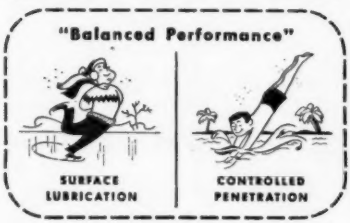

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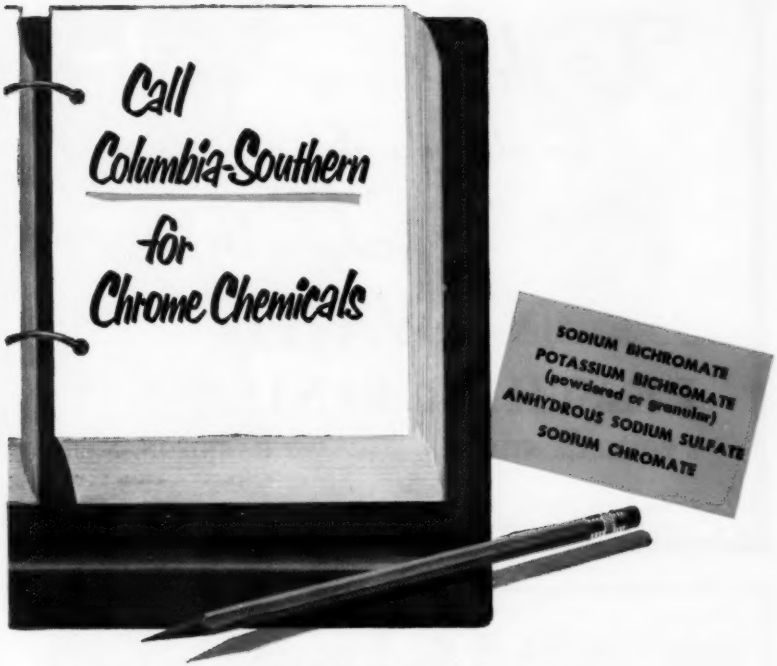

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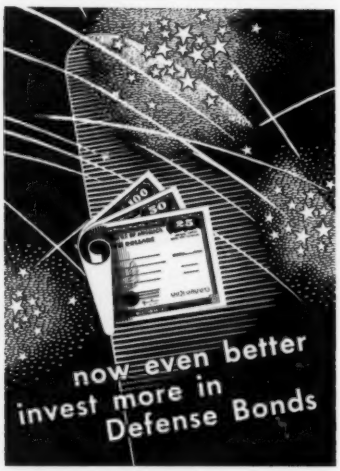

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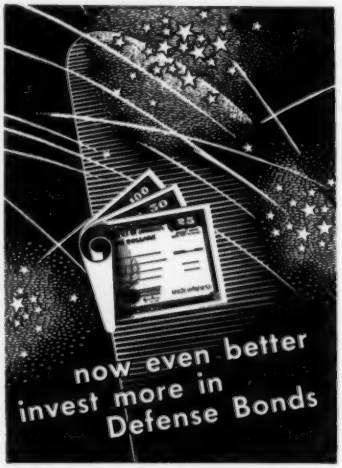

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Solid — Powder — Spray Dried

also

MELLOWED CHESTNUT

Highly Soluble — Weight Giving — Good Color

MADE FROM LIVE WOOD

TYPICAL A.L.C.A. ANALYSIS

	Solid	Mellowed Powder	Spray Dried
TANNIN	61.72	65.95	73.5
NON-TANNIN	21.65	26.67	19.1
INSOLUBLES	.65	.67	.7
WATER	15.98	6.71	6.7

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A TANNING EXTRACT

made from the wood of an Australian species of the Eucalyptus family. It contains both catechol and pyrogallol tannin, the latter predominating.

TYPICAL A.L.C.A. ANALYSIS

	Ordinary	Clarified
TANNIN	61.55	64.34
NON-TANNIN	16.03	17.14
INSOLUBLES	1.70	0.72
WATER	20.72	17.80

Also Available as Liquid with 30% Tannin

As a retanning agent for chrome tanned leather, Myrtan possesses many advantages, such as smooth and strong grain, good color and break, as well as a round feel.

Blended into sole leather tannages, it has given better yields and improved color.

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